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A NEW HOLMIUM ACTIVITY, ^{159}Ho*

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(*Received* 21 *November* 1957)

Abstract—A new activity, ^{159}Ho, has been produced by an (α,4*n*) reaction on stable terbium. The nuclide decays primarily by electron capture with a half-life of 33 min. Evidence has been found to support the proposal by MIHELICH and co-workers that the ground state of ^{160}Ho is short-lived compared to its metastable state whose half-life is 5 hr. The half-life of the ground state seems to be about 28 min.

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BOMBARDMENT by α-particles of terbium in the Berkeley 60-in. cyclotron has resulted in the discovery and mass-assignment of a new isotope, ^{159}Ho. The new activity was seen in a full energy (48 MeV) helium-ion bombardment, but was absent in an experiment that was carried out at 37 MeV. The latter energy is below the (α,4*n*) threshold. This information leads one to believe that the new activity must have been made by such a reaction on terbium. Because the element consists of a single stable isotope, ^{159}Tb, the nuclide observed must be ^{159}Ho.

EXPERIMENTAL

The terbium was irradiated in the form of Tb_2O_3. The powder was placed in a platinum "hat" which fitted into a standard target assembly. A platinum foil was placed over the "hat", and the thickness of the foil was varied to allow bombardment by impinging α-particles of different energies.

The rare earths were separated from one another by an ion-exchange method described elsewhere.[1] After elution, the holmium fraction was studied for total radioactivity in a Geiger counter and for X-ray and γ-radiation in a 100-channel NaI (Tl) scintillation spectrometer.

RESULTS

The resolution of the Geiger counter decay curves yielded only two activities in each of the two bombardments (48 MeV and 37 MeV α-particles on ^{159}Tb), one short-lived and the other having a 5 hr half-life. The short-lived activity was resolved to have a 33 ± 3 min half-life in the full-energy bombardment and a 28 ± 3 min half-life in the second case. When the two shorter activities were compared in abundance relative to the amount of the 5 hr nuclide seen in each case, it was found that the 28 min one was present in a much smaller quantity. The factor between them was at least 30.

The γ-spectra obtained at the two different bombarding energies are shown in Figs. 1 and 2. It is readily noticed that there are four photon peaks present in the full-energy bombardment that are absent in the second experiment. The energies of

* This work was done under the auspices of the U.S. Atomic Energy Commission.

[1] S. G. THOMPSON, B. G. HARVEY, G. R. CHOPPIN and G. T. SEABORG, *J. Amer. chem. Soc.* **76**, 6229 (1954).

the four transitions are: 125, 180, 250, and 305 keV. The rest of the spectrum is identical to the one obtained in the 37 MeV bombardment, except that in Fig. 2 there is a 200 keV transition that is missing in Fig. 1. This particular γ-ray does appear in the full-energy bombardment after the 180 keV photon decays. The energies of the transitions shown in Fig. 2 are 90, 200, 650, 730, 890, and 970 keV. The γ-transitions have been seen by others[2,3,4] and assigned to ^{160}Ho.

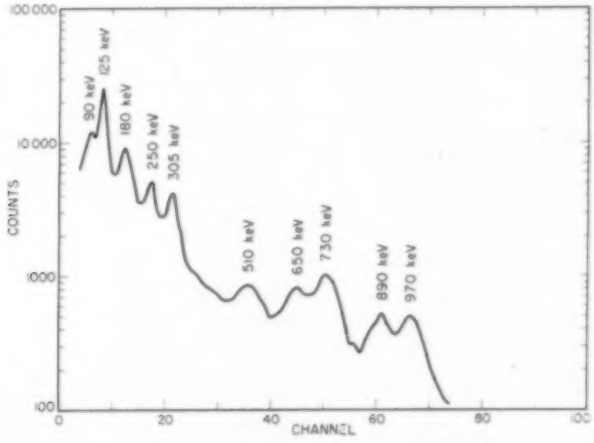

FIG. 1.—Gamma spectrum obtained at 48 MeV.

From the evidence presented, one can draw the following conclusion: an activity that had at least four characteristic γ-rays was seen in the holmium fraction at full bombarding energy. Each of the photopeaks decayed with a half-life of about 33 min. The four γ-transitions were missing in the holmium fraction when the experiment was carried out below the $(\alpha,4n)$ threshold. The new activity must therefore be ^{159}Ho.

The half-lives associated with all the photopeaks will now be discussed because some interesting conclusions can be drawn about ^{160}Ho and ^{160m}Ho. The γ-rays belonging to ^{159}Ho, as mentioned above, decayed with a 33 min half-life. The remainder of the γ-rays shown in Fig. 1 decayed at first with a somewhat similar half-life. A few hours after bombardment time, however, a 5 hr component appeared in the decay of these γ-rays. The explanation was first proposed that all the γ-transitions seen immediately after chemical separation (Fig. 1) belonged to ^{159}Ho. Then a few hours later, when this short-lived isotope had decayed, ^{160}Ho (produced in sufficient amount by an $(\alpha,3n)$ reaction on ^{159}Tb) was seen, as evidenced by the 5 hr component and the isotope's characteristic γ-rays. That a number of γ-rays presumably belonging to ^{159}Ho were similar in energy to transitions assigned to ^{160}Ho by other workers was thought to be a coincidence.

The explanation was found to be incorrect, because in the second bombardment only the four transitions (125, 180, 250, and 305 keV) were absent. One other

[2] W. E. NERVIK and G. T. SEABORG, *Phys. Rev.* **97**, 1092 (1955).
[3] T. H. HANDLEY, *Phys. Rev.* **94**, 945 (1954).
[4] J. W. MIHELICH, B. HARMATZ and T. H. HANDLEY, *Nuclear Spectroscopy of Neutron-Deficient Rare Earths* (Tb through Hf) *ORNL*-63M57, (1957); *Phys. Rev.* **108**, 989 (1957).

difference was the appearance of a 200 keV photopeak in place of the 180 keV one. All of the γ-rays shown in Fig. 2 decayed with the same short half-life and again had a 5 hr component. Because the experiment was carried out below the $(\alpha,4n)$ threshold, ^{159}Ho could not have been made, and so these γ-rays could not belong to ^{159}Ho. Rather they had to be assigned to ^{160}Ho in spite of their initial short half-lives. Also the energies of the photopeaks did not change as the 5 hr component appeared.

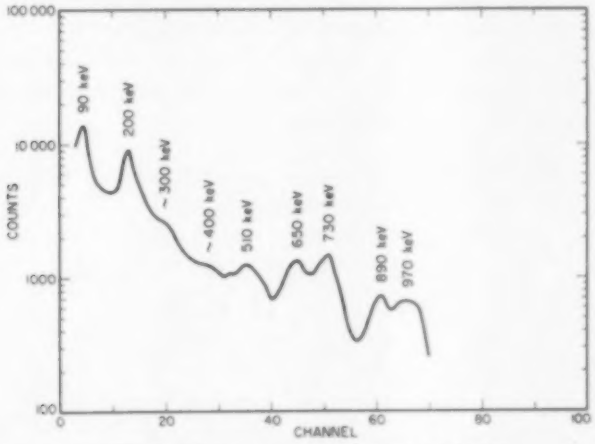

FIG. 2.—Gamma spectrum obtained at 37 MeV.

Therefore, it seemed reasonable to assume that the short half-life (28 min) and the 5 hr one belonged to one and the same isotope.

MIHELICH *et al.* in a recent paper[4] found that ^{160}Ho had a metastable state whose half-life was 5 hr and which decayed to the ground state by an $E3$ transition of 60·1 keV. Their conversion-electron spectra showed no evidence of growth in the intensities of transitions converting in dysprosium. The decay rate of these lines seemed to be identical to that for the lines of the 5 hr metastable state. They proposed two alternatives: (a) either there was no electron capture from the isomeric state and the ground state had a short half-life, or (b) the isomeric state underwent electron capture to levels in ^{160}Dy, in which case the half-life of the ground state was either short or very long compared to 5 hr, or it was 5 hr. They preferred the first alternative. They also suggested that the half-life of the ground state was 22 min as reported by HANDLEY.[3]

Our data certainly support the first alternative. We believe that the short half-life seen in the decay of the transitions of 90, 200, 650, 730, 890, and 970 keV is that of the ground state of ^{160}Ho. In the bombardments, both of the isomers were produced but predominantly the short-lived ground state. The 60·1 keV transition in holmium would be obscured by the K X-ray peak. Then as most of the ground state decayed and as the two activities came into equilibrium, the 5 hr isomer would become noticeable because it would now be controlling the half-lives of the γ-transitions. It should be indicated that our results show the ground state to have a half-life of about 28 ± 3 min rather than 22 min as reported by HANDLEY.

One other piece of information should be added. The resolution of the K X-ray

peak decay curve in the second experiment yielded a 2·5 hr component. This activity is ^{161}Ho. It was not seen in the full-energy experiment. Also a 20 keV γ-ray was seen in the lower-energy bombardment and not at full energy. It is not shown in Fig. 2 but was seen in another energy setting of the γ-analyser. Its half life was 2·5 hr, so it presumably belongs to ^{161}Ho as has been previously suggested by MIHELICH *et al.*[4]

The cross-section for the (α,2n) product, ^{161}Ho, at 48 MeV must be rather low because the isotope was not observed at that particular energy. Analogously then, one would not expect from cross-section systematics to observe the (α,n) product, ^{162}Ho, at either 48 or 37 MeV. The statement is certainly borne out experimentally by the fact that the 67 min half-life of ^{162}Ho was not present in any of the decay curves at either of the two bombarding energies.

Acknowledgement—I should like to express my appreciation to Professor J. O. RASMUSSEN for the constant interest and guidance shown during these and other studies.

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THE SZILARD–CHALMERS REACTION IN FERRICINIUM PICRATE*

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Abstract—The products of the Szilard–Chalmers reaction in ferricinium picrate have been separated by solvent extraction. For samples irradiated in the centre of the Brookhaven reactor about 2·4 per cent of the ^{59}Fe activity was found in the form of parent compound and about 69 per cent as inorganic iron. The quantitative distribution of the ^{59}Fe was not altered by heating the irradiated crystals. An explanation of these results is offered in terms of the reactions undergone by the fragments produced in the solid during the irradiation and the nature of the crystal.

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THE Szilard–Chalmers reaction in ferrocene has recently been investigated.[1] For samples irradiated in the center of the Brookhaven reactor, about 12 per cent of the ^{59}Fe activity was found in the form of the parent compound. The yield was increased to about 21 per cent by heating the irradiated crystals. We have studied the Szilard–Chalmers reaction in ferricinium picrate in order to determine the fate of the radioactive iron and the presence of any effects ascribable to the anion or the crystal structure of the compound.

EXPERIMENTAL

The ferricinium picrate was prepared from ferrocene, picric acid and quinone in benzene solution and purified by recrystallization from water-acetone mixtures.

About 1 g of ferricinium picrate was sealed off *in vacuo* in silica ampoules for irradiation in the water-cooled facility of the Brookhaven reactor at a thermal neutron flux of $3{\cdot}5 \times 10^{12}$ neutrons/cm^2 sec^{-1}.

After irradiation and subsequent annealing, the sample was separated into various fractions by solvent extraction. The radioactivity of each fraction was determined by counting the solution with a glass-walled G–M counter of the immersion type as previously described.[1]

The fractionations were carried out as follows. The irradiated samples were dissolved in 25 ml of 0·1 N HCl containing about 200 mg of ferric chloride. Since a few particles usually remained undissolved the solution was filtered, and the residue dissolved in acetone. The aqueous solution was then extracted with hexane. It was found that considerable activity was recoverable from the walls of the separating funnel by washing with acetone.

Silicotungstic acid was added to an aliquot of the aqueous extract to precipitate ferricinium silicotungstate, which was centrifuged off and converted to the perchlorate by shaking with concentrated perchloric acid. The silicotungstic acid produced was centrifuged off and the ferricinium ion reduced to ferrocene with stannous chloride. The ferrocene was extracted into hexane, and its specific activity determined. It was

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[1] N. SUTIN and R. W. DODSON, *J. inorg. nucl. Chem.* **6**, 91 (1958).

then oxidized to ferricinium with silver sulphate and dilute sulphuric acid and the cycle repeated. The specific activity of the ferrocene at the end of the second cycle usually agreed to within 2 per cent of its previous value.

The free iron in the aqueous extract was determined by extraction from 8 N HCl into *iso*propyl ether and back extraction of the ferric chloride into water.

RESULTS AND DISCUSSION

As a result of the above procedure, activity measurements were obtained on three crude fractions of the sample: a water soluble fraction, a hexane soluble fraction and a fraction insoluble in hexane or water but soluble in acetone. We take the sum of these as the total activity of the sample. The hexane layer generally contained less than 0·1 per cent of the total activity while the acetone fraction contained about 15 per cent of the total activity of the sample. The compounds present in the hexane and acetone fractions have not been identified.

An analysis of a sample irradiated for 4 days at an average flux of $3{\cdot}4 \times 10^{12}$ thermal neutrons/cm^2 sec^{-1} is given in Table 1. For comparison an analysis of a sample of ferrocene irradiated under similar conditions is included in this table.

TABLE 1.—PERCENTAGE OF TOTAL ACTIVITY

	Ferricinium picrate	Ferrocene
Aqueous layer	79·9	53·8
Hexane layer	0·1	25·1
Acetone fraction	20·0	21·1
Ferric chloride	69·5	49·2
Ferricinium picrate	2·2	—
Ferrocene	—	12·8

The quantitative distribution of the ^{59}Fe in the irradiated ferricinium picrate was not significantly altered by annealing at 50°C for one week or 75°C for 18 hr. For samples irradiated for 8 hr, $2{\cdot}4 \pm 0{\cdot}1$ per cent of the ^{59}Fe activity was found in the form of the ferricinium ion and $78{\cdot}5 \pm 1{\cdot}0$ per cent as inorganic iron.

The yield of the radioactive parent compound obtained in the irradiation of ferricinium picrate is considerably less than that obtained in the irradiation of ferrocene. This observation is consistent with the model proposed for ferrocene. It is again postulated that the original molecule is disrupted in practically all the neutron captures. The radioactive ferricinium ion is then formed as a result of the recombination of the recoil species with *cyclo*pentadienyl radicals or ions produced during the slowing-down process or in an exchange of the recoiling iron, before it has become thermalized with a ferricinium ion. On this view the lower yield of ferricinium picrate as compared to ferrocene is not surprising. The recoiling iron will lose energy in collisions with the picrate ion and this will leave less energy for the production of *cyclo*pentadienyl groups. Moreover it is likely that the picrate ion will interfere with recombination reactions between the recoil species and *cyclo*pentadienyl radicals. If part of the radioactive ferricinium arises from exchange reactions with the ferricinium ion during

the slowing-down process electrostatic factors will hinder such reactions as compared to the ferrocene system providing the recoiling iron carries a positive charge.

Similar conclusions about the lower yield of radioactive parent compound obtained in the irradiation of ferricinium picrate follow from a consideration of their crystal types. More energy is lost to the lattice when the recoiling atom slows down in an ionic rather than in a molecular crystal,[2] and this will lead to the production of fewer collision fragments in the former crystal type. In addition the lifetime of the hot zone is shorter in ionic than in molecular crystals and thus hot reactions will have less time to occur in ionic crystals.[2] Similar considerations can account for the higher yield of inorganic iron obtained in the irradiation of ferricinium picrate.

The decrease in the yield of inorganic iron with the length of the irradiation is similar to the results obtained with ferrocene. The model proposed there ascribes the lowering in yield to reactions between the radioactive iron and fragments produced in the decomposition of the ferricinium picrate by the fast neutrons and γ-radiation in the reactor.

The lack of annealing in ferricinium picrate is in marked contrast to the behaviour of ferrocene. The difference in their annealing properties may be due to the interference of the picrate ion with the thermally induced recombination reactions as well as the production of a smaller number of collision fragments and the higher activation energies for diffusion in the ionic lattice.

[2] G. Harbottle and N. Sutin, *J. phys. Chem.* In press.

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VALENCE-STATES IN TITANIUM AND VANADIUM

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Abstract—The energies of excitation from the ground-state to the valence-states deriving from the configurations d^5, d^4s, d^4p, d^3sp, d^3p^2, d^2sp^2, d^2p^3, and dsp^3, of vanadium, and to the valence-states deriving from d^4, d^3s, d^3p, d^2sp, d^2p^2, dsp^2, dp^3, and sp^3 of titanium, have been calculated on the basis of the Slater–Condon theory of atomic spectra, using empirically determined atomic spectral parameters. The relative suitability of each of these alternative valence-states towards the formation of compounds VX_5, and TiX_4, has been assessed from consideration of the excitation energies required, the "bonding-power" of the orbitals, and the geometric stability of the molecular structure formed. It is concluded that the favoured structures are the trigonal bipyramid for VX_5 (deriving essentially from the d^3sp configuration of V), and the tetrahedral structure for TiX_4 (deriving essentially from the d^3s configuration of Ti).

However, it appears that a vanadium atom in an "isovalent hybrid" configuration, obtained by admixing d^3sp with dsp^3, has greater "bonding power" than either of the pure configurations. Similarly, the admixture of d^3s with sp^3 in titanium results in a tetrahedral atom of enhanced orbital bonding power. The mixing process requires a promotional energy, but substantial increases in orbital bonding power result from a small amount of isovalent hybridization, for which the cost in energy is comparatively minor.

The variable dissociation energies in the stepwise disruption of $TiCl_4$ are tentatively discussed in relation to proposed valence configurations of Ti in $TiCl_4$, $TiCl_3$, $TiCl_2$, and TiCl. It is suggested that the excitation energies to reach the valence-states fall along the series $TiCl_4 \rightarrow TiCl$, and that, simultaneously, the effective electronegativity of the Ti atom decreases.

IN previous papers,[1,2] results were given of some calculations on the valence-state excitation energies of several elements, including titanium and vanadium. Our present purpose is to examine more completely the valence-states belonging to these latter two elements. There are eight alternative valence-states available to the vanadium atom in its pentavalent compounds, namely those derived from d^5, d^4s, d^4p, d^3sp, d^3p^2, d^2sp^2, d^2p^3, and dsp^3: the problem is to decide which, among these alternatives, are important or dominant in the valence bonding of vanadium. Similarly, there are eight valence-states available to the titanium atom in its tetravalent compounds, namely those from d^4, d^3s, d^3p, d^2sp, d^2p^2, dsp^2, dp^3, and sp^3.

Among the factors determining the suitability of a given valence-state towards the formation of a stable chemical compound are:

(i) the excitation energy required to achieve the valence-state,

(ii) the "bonding-power" of the atomic orbitals belonging to the valence-state, and (iii) the "geometrical stability" of the structure formed from the valence-state. For example, we may consider the trivalent boron atom, generally accepted to derive from the trigonal configuration sp^2. An alternative arrangement is p^3, but this is less satisfactory than sp^2 with respect to each of the three factors mentioned above. The valence-state excitation energy to form V_3, sp^2, $h_1h_2h_3$ (where h_i is an sp^2 hybrid orbital) in boron is calculated to be 4·49 eV, whereas to reach V_3, p^3, xyz,

[1] H. A. SKINNER, *Trans. Faraday Soc.* **51**, 1036 (1955).
[2] H. A. SKINNER and F. H. SUMNER, *J. inorg. nucl. Chem.* **4**, 245 (1957).

requires 12·77 eV. The "bonding-power" of the trigonal hybrids from V_3, sp^2, is greater than that of *p*-bonds, by the criterion of bonding power introduced by PAULING,[3] or by the overlap criterion preferred by MULLIKEN[4] and later workers.[5] The "geometrical-stability" of the trigonal planar sp^2 structure is expected to be greater than that of the trigonal pyramid p^3 structure because of the greater steric repulsions between non-bonded atoms in the latter case. Finally, it is possible in the sp^2 configuration for the vacant *p*-orbital to be used for back-co-ordination in trivalent boron compounds thus further favouring this structure. The geometrical arrangement in BX_3 molecules is known to be trigonal planar in accordance with sp^2 valence-bonding by the boron atom.

The valence-state of an atom in a molecule must be defined with reference to a particular theory of chemical binding; in this work and in general it is applied to the case where the molecular wave function is of the valence-bond or perfect pairing type built from atomic orbitals. The valence-state is then the state of an atom in a molecule where the valence electrons are placed in specified atomic orbitals, which may be hybridized, with randomized or indeterminate spins. Such a non-stationary state of an atom can be expressed as a mixture of stationary spectroscopic states, e.g. MOFFITT,[6] and the excitation energy calculated from observed spectral terms. An equivalent method of calculating valence-state excitation energies is by means of the coulombic and exchange integrals of the Slater–Condon theory of atomic spectra,[7] and this is a more convenient method when *d*-orbitals are involved. In favourable cases for which the atomic spectra have been investigated and analysed sufficiently the parameters in the Slater equations can be evaluated empirically and the valence-state energies calculated with reasonable accuracy. On the other hand, the quantitative evaluation of "bonding-power" and of "geometrical stability" involve more uncertain procedures. The postulate by PAULING[3] that the bond-forming power of an orbital is proportional to the maximum value of the orbital angular function has the merit of simplicity and has been of great value in providing explanations of the facts of stereochemistry. It lacks, however, a sound quantitative basis,[8,9] and its applicability to the case of hybrids formed from *s*-, *p*-, and *d*- orbitals has been criticized.[5] The status of the overlap integral as a criterion of bond strength[4] stands perhaps a little higher in theory than the measure used by PAULING, but in practice it remains questionable whether the overlap criterion has pronounced advantages.[5] There is room for improvement in the methods used, but here comparative rather than absolute evaluations have been sought. A quantitative evaluation of the interactions between the non-bonded atoms in a molecule is a study which has received very little attention. VAN VLECK[10] has described an approximate treatment which can be applied to non-bonded hydrogen atom interactions. BAUGHAN[11] has described a method of computing

[3] L. PAULING, *J. Amer. chem. Soc.* **53**, 1367 (1931).
[4] R. S. MULLIKEN, *J. phys. Chem.* **56**, 245 (1952).
[5] D. P. CRAIG, A. MACCOLL, R. S. NYHOLM, L. E. ORGEL and L. E. SUTTON, *J. chem. Soc.* 332 (1954).
[6] W. MOFFIT, *Rep. Progr. Phys.* **17**, 173 (1954).
[7] J. C. SLATER, *Phys. Rev.* **34**, 1293 (1929): E. U. CONDON and G. H. SHORTLEY, *Theory of Atomic Spectra*. Cambridge Univ. Press (1935).
[8] H. O. PRITCHARD and H. A. SKINNER, *J. chem. Soc.* 945 (1951).
[9] A. MACCOLL, *Trans. Faraday Soc.* **46**, 369 (1950).
[10] J. H. VAN VLECK, *J. chem. Phys.* **2**, 22 (1934).
[11] E. C. BAUGHAN, *Quart. Rev.* **7**, 103 (1953).

steric repulsion energies where the interactions have been treated in terms of the Lennard–Jones potential. The latter treatment can be used for non-bonded halogen atoms and has been used here for comparing the relative stabilities of different geometrical configurations.

THE EVALUATION OF PARAMETER VALUES

Ti(I), *Table* 1

The values of $A(d^3p)$, $A(d^2sp)$, $F_2{}^{pd}$, $G_1{}^{pd}$, $G_3{}^{pd}$ and $G_1{}^{sp}$ have been taken from ROHRLICH[12] and those for $A(d^4)$, $A(d^3s)$ and $A(d^2s^2)$ taken from MANY.[13] B, C, and $G_2{}^{sd}$ are the means of the values given by ROHRLICH and MANY. $A(d^2p^2)$ and $F_2{}^{pp}$ have been derived, using the Slater procedure, from the observed ^5G and ^5F term values belonging to this configuration in the Ti(I) spectrum, as given by MOORE.[14]

Ti(II), *Table* 1

The values of $A(d^3)$, $A(d^2s)$, $A(ds^2)$ and $G_2{}^{sd}$ have been taken from MANY[13] and those for $A(d^2p)$, $F_2{}^{pd}$, $G_1{}^{pd}$ and $G_3{}^{pd}$ are from RACAH.[15a] B and C are the means of the values given by RACAH and MANY. $A(dsp)$ has been derived from the ^2D and ^2F terms belonging to this configuration, and $G_1{}^{sp}$ from the ^4D, ^4P, terms; but, as RACAH[15b] has pointed out, the ^2P and ^4P terms are inverted from the theoretically predicted order, so the derived values are uncertain. $F_0{}^{pp}$ has been estimated from the approximate relation, $(F_0{}^{ss} - 2F_0{}^{sp} + F_0{}^{pp}) = 0$, and $F_2{}^{pp}$ estimated by extrapolation from values for neighbouring elements.

Ti(III), *Table* 1

The values of $A(d^2)$, $A(dp)$, B, C, $F_2{}^{pd}$ $G_1{}^{pd}$ and $G_3{}^{pd}$ are taken from CADY[16] and expressed in the notation due to RACAH. $A(sd)$ and $G_2{}^{sd}$ have been derived from the ^3D and ^1D terms in the Ti(III) spectrum belonging to this configuration as given by MOORE. $F_0{}^{ss}$ has been estimated.

V(I), *Table* 2

SCHWEIZER[17] has made a least-squares fit, using RACAH's formulae, of the known spectroscopic states belonging to d^5, d^4s and d^3s^2 in the V(I) spectrum, thus deriving the values of $A(d^5)$, $A(d^4s)$, $A(d^3s^2)$, B, C, and $G_2{}^{sd}$. $A(d^5)$ is derived from ^6S, d^5 only. $F_2{}^{pd}$, $G_1{}^{pd}$ and $G_3{}^{pd}$ have been estimated by extrapolation of the corresponding values in Sc(II) and Ti(I). $A(d^4p)$ was derived, using the above parameter values, from the ^6F, ^6D, ^4I and ^4H terms belonging to d^4p in the V(I) spectrum as given by MOORE. The Slater treatment was used and the ^6P term neglected. $A(d^3sp)$ and $G_1{}^{sp}$ have been similarly derived from the ^6G, ^6F, ^6D, ^6P and ^6S terms in V(I) belonging to d^3sp, together with the ^4H, ^2H and ^2I terms, although the latter terms have not been identified with certainty. $A(d^3p^2)$ and $F_2{}^{pp}$ have been derived from the only observed term, ^6G, belonging to this configuration in V(I), using the above parameters and the approximate relation $(F_0{}^{ss} - 2F_0{}^{sp} + F_0{}^{pp}) = 0$.

[12] F. ROHRLICH, *Phys. Rev.* **74**, 1372; 1381 (1948).
[13] A. MANY, *Phys. Rev.* **70**, 511 (1946).
[14] C. E. MOORE, *Atomic Energy Levels*. Vols. 1 and 2, Nat. Bur. Stand., Washington D.C. (1948–52).
[15a] G. RACAH, *Phys. Rev.* **62**, 438 (1942); [b] *Ibid.* **62**, 523 (1942).
[16] G. CADY, *Phys. Rev.* **43**, 322 (1933).
[17] A. A. SCHWEIZER, *Phys. Rev.* **80**, 1080 (1950).

TABLE 1.—PARAMETER VALUES IN Ti(I), Ti(II) AND Ti(III) IN cm^{-1}

Titanium (I)		Titanium (II)		Titanium (III)	
$A(d^4)$	38070	$A(d^3)$	9872	$A(d^2)$	5797
$A(d^3s)$	18299	$A(d^2s)$	9303	$A(pd)$	79404
$A(d^3p)$	37972	$A(d^2p)$	37870	$A(sd)$	41704
$A(d^2s^2)$	5196	$A(dsp)$	64038	F_0^{ss}	(80,000)
$A(d^2sp)$	30491	$A(ds^2)$	25100	F_2^{pd}	444
$A(d^2p^2)$	58761	F_0^{pp}	(66600)	B	694
B	563	F_2^{pp}	700	C	2912
C	1995	B	660	G_2^{sd}	3427
F_2^{pp}	612	C	2240	G_1^{pd}	435
F_2^{pd}	281	F_2^{pd}	290	G_2^{pd}	15
G_1^{sp}	4834	G_1^{sp}	7893		
G_2^{sd}	1336	G_2^{sd}	1824		
G_1^{pd}	306	G_1^{pd}	332		
G_2^{pd}	0	G_2^{pd}	6		

$A(d^4) = 6A$
$A(d^3s) = 3F_0^{sd} + 3A$
$A(d^3p) = 3F_0^{pd} + 3A$
$A(d^2s^2) = F_0^{ss} + 4F_0^{sd} + A - 2G_2^{sd}$
$A(d^2sp) = F_0^{sp} + 2F_0^{sd} + 2F_0^{pd} + A$
$A(d^2p^2) = 4F_0^{pd} + F_0^{pp} + A$
$A = F_0^{dd} - 49F_4^{dd}$
$B = F_2^{dd} - 5F_4^{dd}$
$C = 35F_4^{dd}$

$A(d^3) = 3A$
$A(d^2s) = 2F_0^{sd} + A$
$A(d^2p) = 2F_0^{pd} + A$
$A(dsp) = F_0^{sp} + F_0^{sd} + F_0^{pd}$
$A(ds^2) = 2F_0^{sd} + F_0^{ss} - G_2^{sd}$
$A(d^2) = A$
$A(dp) = F_0^{pd}$
$A(sd) = F_0^{sd}$

Ionization potentials in eV: Ti(I) 6·83, Ti(II) 13·57, Ti(III) 28·14. Ti(IV) 43·24

TABLE 2.—PARAMETER VALUES IN V(I) IN cm^{-1}

$A(d^5)$	40432	F_2^{pp}	3106
$A(d^4s)$	19025	F_2^{pd}	(200)
$A(d^4p)$	40638	G_1^{sp}	11806
$A(d^3s^2)$	10269	G_2^{sd}	1307
$A(d^3sp)$	45322	G_1^{pd}	(300)
$A(d^3p^2)$	76456	G_2^{pd}	(0)
B	578		
C	2273		

$A(d^5) = 10A$
$A(d^4s) = 4F_0^{sd} + 6A$
$A(d^4p) = 4F_0^{pd} + 6A$
$A(d^3s^2) = F_0^{ss} + 6F_0^{sd} + 3A - 3G_2^{sd}$
$A(d^3sp) = F_0^{sp} + 3F_0^{sd} + 3F_0^{pd} + 3A$
$A(d^3p^2) = F_0^{pp} + 6F_0^{pd} + 3A$
$A = F_0^{dd} - 49F_4^{dd}$
$B = F_2^{dd} - 5F_4^{dd}$
$C = 35F_4^{dd}$

In the above tables, the F_0^{ss} and F_0^{sp} parameters are related to the Slater–Condon $\mathscr{F}_0$'s, and $I(nl)$ core-integrals, as follows:—

Titanium I: $F_0^{ss} = \mathscr{F}_0^{ss} + 2I(x)/3$
$F_0^{sp} = \mathscr{F}_0^{sp} + (I(x) + I(y))/3$
Titanium II: $F_0^{ss} = \mathscr{F}_0^{ss} + I(x)$
$F_0^{sp} = \mathscr{F}_0^{sp} + (I(x) + I(y))/2$
Titanium III: $F_0^{ss} = \mathscr{F}_0^{ss} + 2I(x)$
$F_0^{sp} = \mathscr{F}_0^{sp} + I(x) + I(y)$
Vanadium I: $F_0^{ss} = \mathscr{F}_0^{ss} + I(x)/2$
$F_0^{sp} = \mathscr{F}_0^{sp} + (I(x) + I(y))/4$

VALENCE-STATE FORMULAE

The valence-state formulae given below were obtained by the procedure described by VAN VLECK[10] in his discussions of the valence-state of the carbon atom. The symbolism adopted to describe atomic orbital wave functions is:

$$p_x = x;\quad p_y = y;\quad p_z = z$$

$$d_z^2 = \sigma;\quad d_{xz} = \pi;\quad d_{yz} = \pi';\quad d_{x^2-y^2} = \delta;\quad d_{xy} = \delta'$$

where the $d - (xyz)$ functions are written in the notation of EYRING *et al.*[18] The three p-orbitals are equivalent as shown by the interrelations of the integrals;

$$J_{zz} = J_{xx} = J_{yy} = J_{00};\ J_{xy} = J_{yz} = J_{zx} = J_{01};\ \text{and}\ K_{xy} = K_{yz} = K_{zx} = K_{01};^{[19]}$$

where the J's are coulombic interaction integrals and the K's are exchange integrals. The d-orbitals are not equivalent and the relations of the integrals useful in deriving valence-state formulae are listed below:

$$J_{\sigma\sigma} = J_{\pi\pi} = J_{\pi'\pi'} = J_{\partial\partial} = J_{\partial'\partial'} = J_{00};\ J_{\sigma\pi} = J_{\sigma\pi'} = J_{01};\ J_{\sigma\partial} = J_{\sigma\partial'} = J_{02};$$

$$J_{\pi\partial} = J_{\pi\partial'} = J_{\pi'\partial} = J_{\pi'\partial'} = J_{12};\ J_{\pi\pi'} = J_{11} - \tfrac{1}{2}K_{-11};\ J_{\delta\delta'} = J_{22} - \tfrac{1}{2}K_{-22};$$

$$K_{\sigma\pi} = K_{\sigma\pi'} = K_{01};\ K_{\sigma\partial} = K_{\sigma\partial'} = K_{02};\ K_{\pi\pi'} = \tfrac{1}{2}K_{-11};\ K_{\partial\partial'} = \tfrac{1}{2}K_{-22};$$

$$K_{\pi\partial} = K_{\pi\partial'} = K_{\pi'\partial} = K_{\pi'\partial'} = \tfrac{1}{2}(K_{12} + K_{-12})$$

It is noteworthy that $J_{\pi\pi'} = J_{\pi\partial}$ and $K_{\pi\pi'} = K_{\pi\partial}$

Also the following relations hold for p–d-interactions:

$$J_{z\sigma} = J_{00};\ J_{z\pi} = J_{z\pi'} = J_{01};\ J_{z\partial} = J_{z\partial'} = J_{02};\ J_{x\sigma} = J_{y\sigma} = J_{10};$$

$$J_{x\pi} = J_{x\pi'} = J_{y\pi} = J_{y\pi'} = J_{11};\ J_{x\partial} = J_{x\partial'} = J_{y\partial} = J_{y\partial'} = J_{12};$$

$$K_{z\sigma} = K_{00};\ K_{z\pi} = K_{z\pi'} = K_{01};\ K_{z\partial} = K_{z\partial'} = K_{02};\ K_{x\sigma} = K_{y\sigma} = K_{10};$$

$$K_{x\pi} = K_{x\pi'} = K_{y\pi} = K_{y\pi'} = \tfrac{1}{2}(K_{11} + K_{-11});\ K_{x\partial} = K_{x\partial'} = K_{y\partial} = K_{y\partial'}$$

$$= \tfrac{1}{2}(K_{12} + K_{-12})$$

(The $x\pi$ and $y\pi$ relations given here differ from those previously given[1] in that the terms have now been separated.)

It is generally possible to vary the degree of hybridization and thus influence the magnitude of the valence-state excitation energy, the "bonding-power" of the orbitals and the angles between the maximum values of the angular functions. Thus the geometrical arrangement of the molecule and the repulsion energy between non-bonded atoms may be altered. For example, let us consider V_5, d^4s, which gives rise to hybrid orbitals (h) of symmetry C_{4v}. The orbitals may be written in terms of an arbitrary mixing parameter, α, as follows:

$$\theta = 0^\circ \qquad\qquad h_1 = (\sin\alpha)s + (\cos\alpha)\sigma$$

$$\theta = \theta^\circ{}_m \qquad \phi = 45^\circ \qquad h_2 = (\tfrac{1}{2}\cos\alpha)s - \tfrac{1}{2}(\sin\alpha)\sigma - \tfrac{1}{2}\pi' - \tfrac{1}{2}\pi + \tfrac{1}{2}\partial'$$

$$\theta = \theta^\circ{}_m \qquad \phi = 135^\circ \qquad h_3 = (\tfrac{1}{2}\cos\alpha)s - \tfrac{1}{2}(\sin\alpha)\sigma - \tfrac{1}{2}\pi' + \tfrac{1}{2}\pi - \tfrac{1}{2}\partial'$$

[18] H. EYRING, J. WALTER and G. E. KIMBALL, *Quantum Chemistry*. Wiley, New York (1944).
[19] R. S. MULLIKEN, *J. chem. Phys.* **2**, 782 (1934).

and similarly h_4 and h_5 may be written, where $\theta = \theta_m$ and $\phi = 225°$ and 315° respectively. θ_m is given by:

$$\tan 2\theta_m = 2\sqrt{2}/(1 + \sqrt{3}\sin\alpha)$$

In the following table is shown the variation with α of θ_m, the orbital strengths Sh_1 and Sh_2 (where S is defined in the Pauling sense as the value of the angular part of the total wave function of the valence electrons) as well as the valence-state excitation energy (*V.E.*) of the vanadium atom and the steric repulsion energy (*R.E.*) as calculated for a hypothetical VCl_5 molecule. (The calculation of the latter two quantities is described in following sections.)

α	θ_m	*R.E.* (eV)	*V.E.* (eV)	Sh_1	Sh_2	$(Sh_1 + 4Sh_2)$
0°	125°15′	54·16	2·385	2·236	2·437	11·984
30°	118°18′	4·00	2·415	2·437	2·418	12·109
45°	115°25′	1·60	2·345	2·288	2·382	11·816
60°	114°16′	1·35	2·178	1·984	2·319	11·260
90°	112°58′	1·13	1·909	1·000	2·108	9·432

As α increases, the steric repulsion and the valence-state excitation energies decrease but simultaneously there is a decrease in the "bonding-power" of the orbitals shown by $(Sh_1 + 4Sh_2)$. Thus the *R.E.* and *V.E.* terms favour a high value of α whereas the S terms favour a value of α about 30°, so that a balance would have to be reached.

In contrast, for V_4, sp^3, for titanium, the steric repulsion and the valence-state excitation energies are a minimum, and the "bonding-power" a maximum, for the regular tetrahedral structure.

In this section, we restrict discussion to the orbitals deriving from "pure" configurations—e.g. the tetrahedral orbitals from V_4, d^3s, or from V_4, sp^3. In a later section, we examine the *isovalent* hybrids resulting from "mixed" configurations, e.g. the tetrahedral orbitals from V_4, sp^nd^{3-n}, where $n \geqslant 0$ and $\leqslant 3$.

V_5 *Valence-states*

We shall consider cases where the five bonds are equivalent, or at most there are only two different bond strengths involved.

(i) V_5, d^5, $(\sigma\pi\pi'\partial\partial')$

Symmetry C_{5v} $(\theta = 110°59', \phi = 0°, 72°, 144°, 216°, 288°)$

Orbitals: $h_1 = -\sqrt{1/5}\sigma - \sqrt{2/5}(\pi - \partial)$

$$h_2 = -\sqrt{1/5}\sigma - \sqrt{2/5}[(\cos 72°)\pi + (\sin 72°)\pi' - (\cos 36°)\partial + (\sin 36°)\partial'] \text{ etc.}$$

Strength: $Sh_1 = 2{\cdot}194$

Valence-state formula: $A(d^5) - 22{\cdot}5B + 5C$

(ii) V_5, d^4s, $(s\sigma\pi\pi'\partial')$

Symmetry C_{4v} ($\theta = 0°$ and θ_m, $\phi = 45°$, 135°, 225°, 315°)

Orbitals: $h_1 = (\sin\alpha)s + (\cos\alpha)\sigma$

$h_2 = \frac{1}{2}(\cos\alpha)s - \frac{1}{2}(\sin\alpha)\sigma - \frac{1}{2}\pi - \frac{1}{2}\pi' + \frac{1}{2}\delta'$

$h_3 = \frac{1}{2}(\cos\alpha)s - \frac{1}{2}(\sin\alpha)\sigma + \frac{1}{2}\pi - \frac{1}{2}\pi' - \frac{1}{2}\partial'$, etc.

θ_m: 125°15′ — 112°58′

Strength: $Sh_1 = 2{\cdot}236 - 2{\cdot}449 - 1{\cdot}000$; $Sh_2 = 2{\cdot}437 - 2{\cdot}108$.

Valence-state formula:

$$A(d^4s) - 13{\cdot}5B + 3C - 2G_2^{sd} + (\tfrac{3}{16} + \tfrac{1}{8}\sin^2\alpha - \tfrac{5}{16}\sin^4\alpha) \times (\Delta_0^{sd} + 4B + 1{\cdot}6C - 4G_2^{sd})$$

where $\Delta_0^{sd} = A(d^3s^2) + A(d^5) - 2A(d^4s) + 1{\cdot}4C + 3G_2^{sd}$

(iii) V_5, d^4p, $(z\sigma\pi\pi'\partial')$

Symmetry C_{4v}, ($\theta = 0°$ and θ_m $\phi = 45°$, 135°, 225°, 315°)

Orbitals: $h_1 = (\sin\alpha)z + (\cos\alpha)\sigma$;

$h_2 = -\frac{1}{2}(\cos\alpha)z + \frac{1}{2}(\sin\alpha)\sigma - \frac{1}{2}\pi - \frac{1}{2}\pi' + \frac{1}{2}\partial'$;

$h_3 = -\frac{1}{2}(\cos\alpha)z + \frac{1}{2}(\sin\alpha)\sigma + \frac{1}{2}\pi - \frac{1}{2}\pi' - \frac{1}{2}\partial'$, etc.

θ_m: 131°42′ — 142°54′ — 142°16′

Strength: Sh_1: $2{\cdot}236 - 2{\cdot}828 - 1{\cdot}732$; Sh_2: $2{\cdot}476 - 2{\cdot}538 - 2{\cdot}178$

Valence-state formula:

$$A(d^4p) - 13{\cdot}5B + 3C + 4F_2^{pd} - 6{\cdot}5G_1^{pd} - 60{\cdot}75G_3^{pd} + (\tfrac{3}{16} + \tfrac{1}{8}\sin^2\alpha - \tfrac{5}{16}\sin^4\alpha\,(\Delta_0^{pd} + 4B + 1{\cdot}6C + 4F_2^{pp}) - (2{\cdot}5F_2^{pd} + 3{\cdot}5G_1^{pd} + 18G_3^{pd})\sin^2\alpha + (2{\cdot}5F_2^{pd} + 5G_1^{pd} + 33{\cdot}75G_3^{pd})\sin^4\alpha$$

where $\Delta_0^{pd} = A(d^3p^2) + A(d^5) - 2A(d^4p) + 1{\cdot}4C$

(iv) V_5, d^3sp $(sz\sigma\partial\partial')$

Symmetry D_{2h} ($\theta = 0°$, 180° and 90°, $\phi = 0°$, 120°, 240°)

Orbitals: Axial, $h_{1,2} = (\sqrt{\tfrac{1}{3}}\cos\alpha)s + (\sqrt{\tfrac{1}{3}}\sin\alpha)\sigma \pm (1/\sqrt{2})z$

Radial $h_3 = (\sqrt{\tfrac{1}{3}}\sin\alpha)s - (\sqrt{\tfrac{1}{3}}\cos\alpha)\sigma + (\sqrt{2/3})\partial$

$h_{4,5} = (\sqrt{\tfrac{1}{3}}\sin\alpha)s - (\sqrt{\tfrac{1}{3}}\cos\alpha)\sigma - (1/\sqrt{6})\partial \pm (1/\sqrt{2})\partial'$

Strength: S(axial): $1{\cdot}932 - 2{\cdot}957 - 2{\cdot}806$; S(radial): $2{\cdot}226 - 2{\cdot}447 - 2{\cdot}159$

Valence-state formula:

$$A(d^3sp) + 0{\cdot}5F_2^{pp} - (4 + \sin^2\alpha)F_2^{pd} - (8 - 2\sin^2\alpha + \tfrac{5}{6}\sin^4\alpha)(B + 0{\cdot}4C) + 4{\cdot}7C - (1 - \tfrac{1}{2}\sin^2\alpha)G_1^{sp} - (1{\cdot}5 + 1{\cdot}5\sin^2\alpha - \tfrac{5}{6}\sin^4\alpha)G_2^{sd} - 2(1 + \sin^2\alpha)G_1^{pd} - \tfrac{1}{2}(57 - 27\ \sin^2\alpha)G_3^{pd} + \tfrac{1}{8}(1 - \sin^2\alpha)\Delta_0^{sp} + \tfrac{1}{8}(3\sin^2\alpha - \tfrac{5}{3}\sin^4\alpha)\,\Delta_0^{sd} + \tfrac{1}{8}\Delta_0^{pd}\sin^2\alpha$$

where $\Delta_0^{sp} = A(d^3s^2) + A(d^3p^2) - 2A(d^3sp) + 3G_2^{sd}$

(v) V_5, d^3p^2, $(xy\sigma\partial\partial')$

Symmetry D_{5h} $(\theta = 90°, \phi = 0°, 72°, 144°, 216°, 288°)$

Orbitals:
$$h_1 = -(1/\sqrt{5})\sigma + (\sqrt{2/5})\,x + (\sqrt{2/5})\partial$$
$$h_2 = -(1/\sqrt{5})\sigma + (\sqrt{2/5})\,[(\cos\ 72°)x + (\sin\ 72°)y - (\cos\ 36°)\partial + (\sin\ 36°)\partial']$$
$$h_3 = -(1/\sqrt{5})\partial + (\sqrt{2/5}) \times [(-\cos 36°)x + (\sin 36°)y + (\cos 72°)\partial - (\sin 72°)\partial'] \text{ etc.}$$

Strength: 2·820

Valence-state formula:

$$A(d^3p^2) - 6{\cdot}8B + 1{\cdot}98C - 2{\cdot}3F_2^{pp} + 3{\cdot}6F_2^{pd} - 9{\cdot}8G_1^{pd} - 92{\cdot}4G_3^{pd} + 0{\cdot}3\Delta_0^{pd}$$

(vi) V_5, d^2sp^2, $(sxy\sigma\partial')$

Symmetry C_{4v} $(\theta = 0°$ and $90°, \phi = 45°, 135°, 225°, 315°)$

Orbitals:
$$h_1 = (\sin\alpha)s + (\cos\alpha)\sigma$$
$$h_2 = \tfrac{1}{2}(\cos\alpha)s - \tfrac{1}{2}(\sin\alpha)\sigma + \tfrac{1}{2}x + \tfrac{1}{2}y + \tfrac{1}{2}\partial'$$
$$h_3 = \tfrac{1}{2}(\cos\alpha)s - \tfrac{1}{2}(\sin\alpha)\sigma - \tfrac{1}{2}x + \tfrac{1}{2}y - \tfrac{1}{2}\partial', \text{ etc.}$$

Strength: Sh_1: 2·236 — 2·449 — 1·000; Sh_2: 2·692 — 2·943 — 2·752

Valence-state formula:

$$A(d^2sp^2) - 2{\cdot}5F_2^{pp} - 6B + 0{\cdot}5C - G_1^{sp} - G_2^{sd} - 5G_1^{pd} - 45G_3^{pd}$$
$$+ \tfrac{1}{8}(1 - \sin^2\alpha)(\Delta_0^{sp} - 4F_2^{pd} - 4G_1^{sp})$$
$$+ \tfrac{1}{16}(1 + 4\sin^2\alpha - 5\sin^4\alpha)(\Delta_0^{sd} + 4B + 1{\cdot}6C - 4G_2^{sd})$$
$$+ \tfrac{1}{8}(1 + \sin^2\alpha)(\Delta_0^{pd} + 4B + 1{\cdot}6C - 4G_1^{pd} - 72G_3^{pd})$$

where $A(d^2sp^2) = 2F_0^{sp} + 2F_0^{sd} + 4F_0^{pd} + F_0^{pp} + A$.

(vii) V_5, d^2p^2, $(xyz\sigma\partial')$

Symmetry C_{4v} $(\theta = 0°$ and $\theta_m, \phi = 45°, 135°, 225°, 315°)$

Orbitals:
$$h_1 = (\sin\alpha)z + (\cos\alpha)\sigma$$
$$h_2 = -\tfrac{1}{2}(\sin\alpha)z + \tfrac{1}{2}(\sin\alpha)\sigma + \tfrac{1}{2}x + \tfrac{1}{2}y + \tfrac{1}{2}\partial'$$
$$h_3 = -\tfrac{1}{2}(\sin\alpha)z + \tfrac{1}{2}(\sin\alpha)\sigma - \tfrac{1}{2}x + \tfrac{1}{2}y - \tfrac{1}{2}\partial', \text{ etc.}$$

θ_m: 105° 40′ — 136° 30′ — 97° 15′

Strength: Sh_1 2·236 — 2·828 — 1·732; Sh_2 2·308 — 1·591

Valence-state formula.

$$A(d^2p^2) - 9F_2^{pp} - 6B + 0{\cdot}5C - 7{\cdot}5G_1^{pd} - 78{\cdot}75G_3^{pd} + 2{\cdot}5F_2^{pd}(\sin^2\alpha - \sin^4\alpha)$$
$$- (\tfrac{11}{2}G_1^{pd} + \tfrac{75}{4}G_3^{pd})\sin^2\alpha + (5G_1^{pd} + \tfrac{27}{2}G_3^{pd})\sin^4\alpha$$
$$+ (\tfrac{3}{16} + \tfrac{3}{8}\sin^2\alpha - \tfrac{5}{16}\sin^4\alpha)(\Delta_0^{pd} + 4F_2^{pp} + 4B + 1{\cdot}6C)$$

where $A(d^2p^2) = 3F_0^{pp} + 6F_0^{pd} + A$

(viii) V_5, dsp^3, $(sxyz\sigma)$

Symmetry D_{3h} ($\theta = 0°$, 180° and 90°, $\phi = 0°$, 120°, 240°)

Orbitals: Axial, $h_{1,2} = (\sqrt{\tfrac{1}{3}}\cos\alpha)\,s + (\sqrt{\tfrac{1}{3}})\sin\alpha)\,\sigma\sin\alpha\sigma \pm (1/\sqrt{2})z$

Radial, $h_3 = (\sqrt{\tfrac{1}{3}}\sin\alpha)\,s - (\sqrt{\tfrac{1}{3}}\cos\alpha)\,\sigma\sin\alpha\sigma + (\sqrt{2/3})x$

$h_{4,5} = (\sqrt{\tfrac{1}{3}}\sin\alpha)\,s - (\sqrt{\tfrac{1}{3}}\cos\alpha)\,\sigma - (1/\sqrt{6})x \pm (1/\sqrt{2})y$

Strength: S(axial) 1·932 — 2·957 — 2·806;

S(radial) 2·059 — 2·280 — 1·992.

Valence-state formula:

$$A(dsp^3) - 9\tfrac{1}{2}F_2^{pp} + \tfrac{1}{2}(2 - 5\sin^2\alpha)F_2^{pd} + \tfrac{1}{6}(4 + 4\sin^2\alpha - 5\sin^4\alpha) \times (B + 0{\cdot}4C) - (2 + \tfrac{1}{6}\sin^2\alpha)\,G_1^{sp} - \tfrac{1}{2}G_2^{sd} - \tfrac{1}{2}(11 + 4\sin^2\alpha)G_1^{pd} - \tfrac{1}{2}(87 + 3\sin^2\alpha)G_3^{pd} + \tfrac{1}{24}\{(3 + \sin^2\alpha)\Delta_0^{sp} + 5(1 - \sin^2\alpha)(\Delta_0^{sd} - 5G_2^{sd})\sin^2\alpha + (4 - \sin^2\alpha)\Delta_0^{pd}\}$$

where $A(dsp^3) = 3F_0^{sp} + F_0^{sd} + 3F_0^{pd} + 3F_0^{pp}$

V_4 *Valence states*

We shall consider cases of four equivalent bonds, or where at most there are only two different bond strengths involved.

(i) V^4, d^4, $(\sigma\pi\pi'\partial')$

Symmetry C_{4v} ($\theta = 113$, $\phi = 45°$, 135°, 225°, 315°)

Orbitals: $h_1 = -\tfrac{1}{2}\sigma - \tfrac{1}{2}\pi - \tfrac{1}{2}\pi' + \tfrac{1}{2}\partial'$

$h_2 = -\tfrac{1}{2}\sigma + \tfrac{1}{2}\pi - \tfrac{1}{2}\pi' - \tfrac{1}{2}\partial'$, etc.

Strength: 2·108

Valence-state formula: $A(d^4) - 13{\cdot}5B + 3C$

(ii) (a) V_4, sd^3, $(s\sigma\pi\pi'\partial\partial')$

Symmetry C_{3v} ($\theta = 0°$ and θ_m, $\phi = 0°$, 120° 240°)

Orbitals: $h_1 = (\sin\alpha)s + (\cos\alpha)\sigma$

$h_2 = (\sqrt{\tfrac{1}{3}}\cos\alpha)s - (\sqrt{\tfrac{1}{3}}\sin\alpha)\sigma + \sqrt{2/3}[(\sin\beta)\partial - (\cos\beta)\pi]$

$h_{3,4} = (\sqrt{\tfrac{1}{3}}\cos\alpha)s - (\sqrt{\tfrac{1}{3}}\sin\alpha)\sigma - \sqrt{1/6}[(\sin\beta)\partial - (\cos\beta)\pi]$

$\pm\sqrt{1/2}\,[(\sin\beta)\partial' + (\cos\beta)\pi']$

θ_m: θ_m is given by $\tan 2\theta_m = \cos\beta/(\sqrt{1{\cdot}5}\sin\alpha + \sin\beta)$

θ_m varies between 90° and 135°

Strength: Sh_1 2·235 — 2·449 — 1·000; Sh_2 2·158 — 2·449 — 2·226

Valence-state formula:

$$A(d^3s) - 1{\cdot}5G_2^{sd} + 1{\cdot}5C + 0{\cdot}5B(15\sin^4\beta - 30\sin^2\beta - 1) + \tfrac{1}{6}(1 + \sin^2\alpha - 2\sin^4\alpha)(\Delta_0^{sd} - 4G_2^{sd} + 4B + 1{\cdot}6C)$$

where $\Delta_0^{sd} = A(d^3s^2) - 2A(d^3s) + A(d^4) + 1{\cdot}4C + 2G_2^{sd}$

(b) V_4, sd^3, $(s\pi\pi'\partial')$

Symmetry T_d ($\theta = 54°44'$ and $125°16'$, $\phi = 45°$, $135°$, $225°$, $315°$)

Orbitals: $h_1 = \frac{1}{2}(s + \pi + \pi' + \partial')$

$h_2 = \frac{1}{2}(s - \pi - \pi' + \partial')$, etc.

Strength: 2·437

Valence-state formula:

$A(d^3s) - 9{\cdot}75B + 1{\cdot}8C - 2{\cdot}25G_2^{sd} + \frac{3}{16}\Delta_0^{sd}$

(iii) V_4, d^3p, $(z\sigma\pi\pi'\partial\partial')$

Symmetry C_{3v} ($\theta = 0°$ and θ_m, $\phi = 0°$, $120°$, $240°$)

Orbitals: $h_1 = (\sin\alpha)z + (\cos\alpha)\sigma$

$h_2 = -(\sqrt{\tfrac{1}{3}}\cos\alpha)z + (\sqrt{\tfrac{1}{3}}\sin\alpha)\sigma + \sqrt{2/3}[(\sin\beta)\sigma - (\cos\beta)\pi]$

$h_{3,4} = -(\sqrt{\tfrac{1}{3}}\cos\alpha)z + (\sqrt{\tfrac{1}{3}}\sin\alpha)\sigma - \sqrt{1/6}[(\sin\beta)\sigma - (\cos\beta)\pi]$
$\pm (1/\sqrt{2})[(\sin\beta)\sigma' + (\cos\beta)\pi']$

For $\beta = 90°$, values of α are not permitted above $30°$

θ_m: $162° - 108°\,26'$

Strength: Sh_1 2·236 — 2·828 — 1·732; Sh_2 2·324 — 2·706 — 1·564

Valence-state formula:

$A(d^3p) + 1{\cdot}5C + 0{\cdot}5B(15\sin^4\beta - 30\sin^2\beta - 1) + 7\tfrac{1}{3}F_2^{pd} - 7G_1^{pd} - 53{\cdot}5G_3^{pd}$
$+ (\tfrac{1}{6} + \tfrac{1}{6}\sin^2\alpha - \tfrac{1}{3}\sin^4\alpha)(\Delta_0^{pd} + 4F_2^{pp} + 4B + 1{\cdot}6C)$
$- (2F_2^{pd} + 3\tfrac{1}{3}G_1^{pd} + 20G_3^{pd})\sin^2\alpha + (2\tfrac{2}{3}F_2^{pd} + 5\tfrac{1}{3}G_1^{pd} + 36G_3^{pd})\sin^4\alpha$
$- 2\,(F_2^{pd} + G_1^{pd} + 3G_3^{pd})\sin^2\alpha\,.\sin^2\beta - 5\,(2F_2^{pd} - G_1^{pd} - 3G_3^{pd})\sin^2\beta$

where $\Delta_0^{pd} = A(d^2p^2) - 2A(d^3p) + A(d^4) + 1{\cdot}4C$

(iv) V_4, d^2sp $(sz\pi\pi'\partial\partial')$

Symmetry C_{3v} ($\theta = 0°$ and θ_m, $\phi = 0°$, $120°$, $240°$)

Orbitals: $h_1 = (\sin\alpha)s + (\cos\alpha)z$

$h_2 = (\sqrt{\tfrac{1}{3}}\cos\alpha)s - (\sqrt{\tfrac{1}{3}}\sin\alpha)z + \sqrt{2/3}[(\sin\beta)\partial - (\cos\beta)\pi]$

$h_{3,4} = (\sqrt{\tfrac{1}{3}}\cos\alpha)s - (\sqrt{\tfrac{1}{3}}\sin\alpha)z - (1/\sqrt{6})[(\sin\beta)\partial - (\cos\beta)\pi]$
$\pm (1/\sqrt{2})[(\sin\beta)\partial' + (\cos\beta)\pi']$

θ_m: $140°\,46' - 90°$

Strength: Sh_1 1·732 — 2·000 — 1·000; Sh_2 2·159 — 2·680 — 1·739

Valence-state formula:

$A(d^2sp) - 0{\cdot}5G_1^{sp} - G_2^{sd} - 3G_1^{pd} - 24G_3^{pd} + 4F_2^{pd} - \frac{4}{3}F_2^{pp}\sin^2\alpha$
$+ \frac{23}{30}C + B(\frac{15}{2}\sin^4\beta - 17/6) + (2F_2^{pp} - \frac{2}{5}F_2^{pd})\sin^2\alpha$
$- 3(4F_2^{pd} - G_1^{pd} - 3G_3^{pd})\sin^2\beta + 2(F_2^{pd} + 3G_3^{pd})\sin^2\alpha\,.\sin^2\beta$
$+ \frac{1}{3}(\sin^2\alpha - \sin^4\alpha)(\Delta_0^{sp} - 4G_1^{sp}) + \frac{1}{6}(\Delta_0^{pd} - 12G_1^{pd} - 96\,G_3^{pd})\sin^2\alpha$
$+ \frac{1}{6}(1 - \sin^2\alpha)(\Delta_0^{sd} - 4G_2^{sd})$

where $\Delta_0^{sp} = A(d^2s^2) - 2A(d^2sp) + A(d^2p^2) + 2G_2^{sd}$

(v) (a) V_4, d^2p^2, $(zx\sigma\pi)$

Symmetry D_{4h} $(\theta = 45°, 135°, 225°, 315°, \phi = 0)$

Orbitals: $h_1 = \frac{1}{2}(z + x + \sigma + \pi)$

$h_2 = \frac{1}{2}(-z + x + \sigma - \pi)$, etc.

Strength: 2·473

Valence-state formula:

$A(d^2p^2) - 2{\cdot}5F_2^{pp} + \frac{27}{8}F_2^{pd} + 2{\cdot}5B + 0{\cdot}9C - 0{\cdot}75(11G_1^{pd} + 93G_3^{pd}) + \frac{1}{4}\Delta_0^{pd}$

(b) V_4, d^2p^2, $(zx\sigma\partial)$

Symmetry: D_{4h} $(\theta = 0°, 90°, 180°, 270°, \phi = 0)$

Orbitals: $h_{1,2} = \pm\sqrt{1/2}z + \sqrt{1/2}\sigma$

$h_{3,4} = \pm\sqrt{1/2}x + \sqrt{1/2}\partial$

Strength: $Sh_{1,2}$: 2·806; $Sh_{3,4}$: 2·594

Valence-state formula:

$A(d^2p^2) - 2{\cdot}5F_2^{pp} - \frac{3}{2}F_2^{pd} - 5B + 0{\cdot}9C - 0{\cdot}5(15G_1^{pd} + 135G_3^{pd}) + \frac{1}{4}\Delta_0^{pd}$

(vi) V_4, dsp^2, $(sxy\partial)$

Symmetry D_{4h} $(\theta = 90°, \phi = 0°, 90°, 180°, 270°)$

Orbitals: $h_{1,2} = (\sqrt{\frac{1}{3}}\sin\alpha)s + (\sqrt{\frac{1}{3}}\cos\alpha)\partial \pm (1/\sqrt{2})x$

$h_{3,4} = (\sqrt{\frac{1}{3}}\cos\alpha)s - (\sqrt{\frac{1}{3}}\sin\alpha)\partial \pm (1/\sqrt{2})y$

Strength: Sh_1 2·594 — 2·693 — 1·932; Sh_2 1·932 — 2·693 — 2·594

The bonds are equivalent at $\alpha = 45°$, $S = 2{\cdot}693$

Valence-state formula:

$A(dsp^2) - 2{\cdot}5F_2^{pp} + 3{\cdot}5F_2^{pd} + 0{\cdot}5B + 0{\cdot}2C - 1{\cdot}5G_1^{sp} - 0{\cdot}5G_2^{sd} - 4{\cdot}5G_1^{pd} - 36G_3^{pd} + \frac{1}{8}(\Delta_0^{sp} + \Delta_0^{pd}) + \frac{1}{4}(\sin^2\alpha - \sin^4\alpha)(\Delta_0^{sd} + 4B + 1{\cdot}6C - 4G_2^{sd})$

where $A(dsp^2) = F_0^{sd} + 2F_0^{pd} + 2F_0^{sp} + F_0^{pp}$

(vii) V_4, dp^3, $(xyz\sigma)$

Symmetry C_{3v} $(\theta = 0°$ and $\theta_m, \phi = 0°, 120°, 240°)$

Orbitals: $h_1 = (\sin\alpha)z + (\cos\alpha)\sigma$

$h_2 = -(\sqrt{\frac{1}{3}}\cos\alpha)z + (\sqrt{\frac{1}{3}}\sin\alpha)\sigma + \sqrt{2/3}x$

$h_{3,4} = -(\sqrt{\frac{1}{3}}\cos\alpha)z + (\sqrt{\frac{1}{3}}\sin\alpha)\sigma - (1/\sqrt{6})x \pm (1/\sqrt{2})y$

θ_m: 125° 15′ — 158° 35′

Strength: Sh_1 2·236 — 2·828 — 1·732; Sh_2 1·732 — 1·906 — 1·449

Valence-state formula:

$$A(dp^3) - \tfrac{21}{2}F_2^{pp} - 3G_1^{pd} - \tfrac{63}{2}G_3^{pd} - (6G_1^{pd} + 48G_3^{pd})\sin^2\alpha + (\tfrac{16}{3}G_1^{pd} + 36G_3^{pd})\sin^4\alpha + 2F_2^{pd}\sin^2\alpha + (\tfrac{1}{2}\sin^2\alpha - \tfrac{1}{3}\sin^4\alpha) \times (\Delta_0^{pd} + 4F_2^{pp} - 8F_2^{pd} + 4B + 1{\cdot}6C)$$

where $A(dp^3) = 3F_0^{pp} + 3F_0^{pd}$

(viii) V_4, sp^3, $(sxyz)$

Symmetry C_{3v} ($\theta = 0°$ and θ_m, $\phi = 0°$, 120°, 240°)

Orbitals:

$$h_1 = (\sin\alpha)s + (\cos\alpha)z$$

$$h_2 = (\sqrt{\tfrac{1}{3}}\cos\alpha)s - (\sqrt{\tfrac{1}{3}}\sin\alpha)z + \sqrt{2/3}\,x$$

$$h_{3,4} = (\sqrt{\tfrac{1}{3}}\cos\alpha)s - (\sqrt{\tfrac{1}{3}}\sin\alpha)z - (1/\sqrt{6})x \pm \sqrt{1/2}\,y$$

θ_m: 90° − 125° 16′ For $\alpha = 30°$, the regular tetrahedral structure is obtained with symmetry *Td*.

Strength: Sh_1: 1·732 — 2·000 — 1·000; Sh_2: 1·992 — 2·000 — 1·732.

Valence-state formula:

$$A(sp^3) - 10{\cdot}5F_2^{pp} - 1{\cdot}5G_1^{sp} + (\tfrac{1}{6} + \tfrac{1}{6}\sin^2\alpha - \tfrac{1}{3}\sin^4\alpha)(\Delta_0^{sp} + 4F_2^{pp} - 4G_1^{sp})$$

where $A(sp^3) = 3F_0^{sp} + 3F_0^{pp}$

STERIC REPULSION ENERGIES

These energies have been computed by the method described by BAUGHAN.[11] The non-bonding potential energy is given by $W = -a/y^6 + \beta/y^{12}$, where y is the distance between the non-bonded atoms. a and β are, in effect, calculated from W_0, the equilibrium van der Waals energy, and Y_0, the equilibrium van der Waals distance. Here we have considered repulsions between chlorine atoms only for which $W_0 = 590$ cal/g atom and $Y_0 = 3{\cdot}54$ Å.[11] For $y > Y_0$, there will be a van der Waals attraction between the atoms which is comparatively trivial and at the most can amount to 1 kcal per bond. For $y < Y_0$, there is steric repulsion. For molecules containing bonds non-equivalently disposed in space, each bond must be treated separately and the effects summed for the molecule.

Calculations have been made for $TiCl_4$ and the hypothetical VCl_5 molecule for the possible geometric structures of these molecules. The bond lengths and force constants were assumed to be constant throughout. For $TiCl_4$, r(Ti–Cl) = 2·18 Å[20] and k_s(Ti–Cl) = 2·46 × 10^5 dynes cm^{-1}.[21] For VCl_5, the (V–Cl) distance was assumed to be 2·1 Å (in VCl_4, r(V–Cl) = 2·03 Å[22] and in $VOCl_3$, r(V–Cl) = 2·11 Å[23]). The force constant, k_s(V–Cl), was calculated from Badger's rule, $k_s(r_e - d_{ij})^3 = C_{ij}$ (with $C_{ij} = 1{\cdot}86 \times 10^5$ and $d_{ij} = 1{\cdot}25$) to be 2·92 × 10^5 dynes cm^{-1}.

The repulsion energies thus calculated have only approximate validity; but when

[20] M. W. LISTER and L. E. SUTTON, *Trans. Faraday Soc.* **37**, 393 (1941).
[21] D. F. HEATH and J. W. LINNETT, *Trans. Faraday Soc.* **44**, 561 (1948).
[22] W. N. LIPSCOMB and A. G. WHITTAKER, *J. Amer. chem. Soc.* **36**, 668 (1940).
[23] K. J. PALMER, *J. Amer. chem. Soc.* **60**, 2360 (1938).

the value is very large,* we may reasonably conclude that the steric factor excludes the structure in considering the valence bonding of the element.

DISCUSSION

Table 3 summarizes the calculations on the V_5 states of vanadium deriving from "pure" configurations. Of these states, d^3p^2, d^2p^3, and dsp^3 have relatively high valence-state excitation energies, and should be not favoured for this reason. The states d^5 and d^4p have moderate excitation energies, but lead to structures in which there is excessive steric repulsion. Of the two remaining states, d^4s is favoured relative to

TABLE 3.—V_5 STATES OF VANADIUM

State	θ	*R.E.* (eV) in VCl_5	*V* (eV)	Sh_1	Sh_2
d^5, C_{5v}	110°59′	163	4·81	2·194	
d^4s, C_{4v}	112°58′	1·13*	1·91*	1·000	2·108
	118°18′	4·00	2·42	2·437*	2·418*
d^4p, C_{4v}	142°16′	945	4·83*	1·732	2·178
	138°41′	701	5·95	2·803*	2·538*
	131°42′	112*	6·10	2·476	2·236
d^3sp, D_{3h}	0°, 90°	0·66	3·78*	1·932	2·226
		0·66	5·19	2·949*	2·414*
d^3p^2, D_{3h}	0°	24·3	9·83	2·830	
d^2sp^2, C_{4v}	90°	0·90	10·32*	2·236	2·692
		0·90	10·78	2·437*	2·905*
d^2p^3, C_{4v}	105°40′	0·80*	15·63*	2·236	2·308
	128°20′	82·6	16·10	2·803*	2·017*
dsp^3, D_{3h}	0°, 90°	0·66	19·02*	2·806	1·992
		0·66	19·27	2·949*	2·247*

* The terms marked thus are the most favourable for that particular state, i.e. the minimum steric repulsion, the minimum valence-state energy, or the maximum "bonding-power".
R.E. = calculated steric repulsion energy between non-bonded Cl atoms in VCl_5
V = excitation energy to achieve the valence-state.

d^3sp by ca. 3 eV in excitation energy, but the latter has higher bonding-power, and less steric repulsion. We conclude that the d^3sp configuration is the most satisfactory of the various alternatives, and that the trigonal bipyramid structure should be found in VX_5 compounds. The structure of VF_5 (the only known pentahalide of vanadium) has not as yet been determined, but the trigonal bipyramid arrangement has been found in the niobium and tantalum pentahalides.[24]

If it is accepted that the trigonal bipyramid structure is the correct one for VX_5 compounds, there are two configurations, d^3sp, and dsp^3, leading to this arrangement, of which d^3sp is apparently much the more satisfactory both in respect of bonding power, and of ease of attainment: however, we have to recognize that an "isovalent" state (built up by mixing d^3sp and dsp^3 in suitable proportions), might have the

* Some of the repulsion energies given in Tables 3 and 4 are very high: these arise in cases where the models require very forced close-approach of the non-bonded chlorine atoms—e.g. in VCl_5, d^4p, C_{4v}, when $\theta = 142°$, the Cl . . . . Cl distance at the base of the pyramid = 1·81 Å, compared with the van der Waals distance of 3·54 Å.

[24] H. A. SKINNER and L. E. SUTTON, *Trans. Faraday Soc.* **36**, 668 (1940).

advantage over both the parent configurations. This isovalent situation is represented by the set of hybrid orbitals below:—

$$h_{1,2} = (\sqrt{\tfrac{1}{3}}\cos\alpha)s \pm (1/\sqrt{2})z + (\sqrt{\tfrac{1}{3}}\sin\alpha)\sigma$$

$$h_3 = (\sqrt{\tfrac{1}{3}}\sin\alpha)s - (\sqrt{\tfrac{1}{3}}\cos\alpha)\sigma + \sqrt{2/3}[(\sin\beta)x + (\cos\beta)\partial]$$

$$h_{4,5} = (\sqrt{\tfrac{1}{3}}\sin\alpha)s - (\sqrt{\tfrac{1}{3}}\cos\alpha)\sigma - \sqrt{1/6}[(\sin\beta)x + (\cos\beta)\partial]$$
$$\pm(1/\sqrt{2})[(\sin\beta)y - (\cos\beta)\partial']$$

where $h_{1,2}$ are the axial, and $h_{3,4,5}$ the radial orbitals: α and β are variable mixing coefficients.

We have calculated the valence-state excitation energies, and the orbital strengths for the range of values of α and β:

VALENCE-STATE ENERGY (eV)

α \ β	0	$\pi/6$	$\pi/4$	$\pi/3$	$\pi/2$
0	3·78	6·89	10·53	14·77	19·58
$\pi/6$	4·32	7·26	10·78	14·89	19·54
$\pi/4$	4·79	7·59	10·96	14·92	19·43
$\pi/3$	5·19	7·85	11·08	14·89	19·26
$\pi/2$	5·53	8·04	11·12	14·78	19·02

ORBITAL STRENGTHS

α \ β	Radial 0	$\pi/6$	$\pi/4$	$\pi/3$	$\pi/2$	Axial
0	2·227	2·722	2·764	2·661	2·060	1·932
$\pi/6$	2·427	2·921	2·964	2·860	2·260	2·628
$\pi/4$	2·446	2·941	2·983	2·880	2·279	2·843
$\pi/3$	2·404	2·899	2·941	2·838	2·237	2·949
$\pi/2$	2·159	2·654	2·695	2·593	1·992	2·806

The extreme values, $\beta = 0$ and $\beta = \pi/2$, represent the pure configurations d^3sp, and dsp^3: the significant point emerges that for intermediate values of β, the orbital strengths of the *radial* bonds may be larger than those given by either of the pure configurations. This is clearly shown by Fig. 1, in which the variation of S (radial) with β, for the particular choice $\alpha = \pi/4$, is plotted: on the same graph, the variation of the valence-state excitation energy with β is also shown. The effect of isovalent hybridization is remarkable: thus the mixture 90% d^3sp, 10% dsp^3, or V_5, $d^{2\cdot8}sp^{1\cdot2}$, produces radial bonds of strength ca. 2·83, compared with 2·45 ($\alpha = \pi/4$) from the pure configuration d^3sp, for a comparatively small additional cost in excitation energy (6 eV against 4·8 eV).

Radial bonds of maximum strength ($S = 2{\cdot}987$) result from the choice $\alpha = \beta = \sin^{-1}(2/3) = 41°48'$, corresponding to the configuration $d^{2\cdot11}sp^{1\cdot89}$. However, the

excitation energy to reach this configuration is in excess of 10 eV, and the advantage of the increased bonding-power is offset by the mounting cost. In short, it would seem to be most profitable for the vanadium atom to adopt a *little* isovalent hybrid character, probably of the order 10 per cent admixture of dsp^3 with d^3sp.

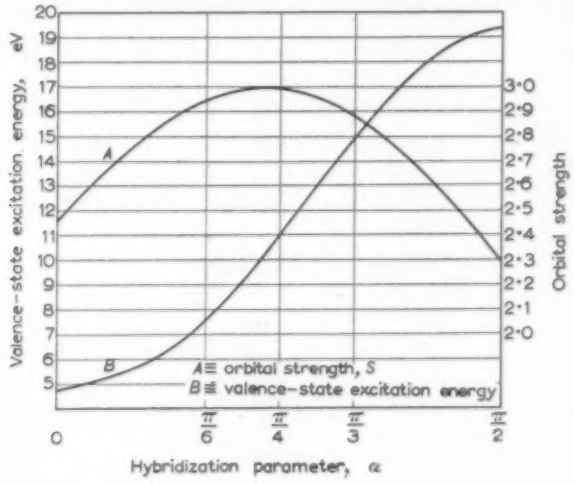

FIG. 1

An examination of Table 4 shows that the configuration d^3s, T_d, of titanium has almost the lowest excitation-energy, with negligible steric repulsion and relatively high bonding-power. It must be an important contributor in tetravalent titanium

TABLE 4.—V_4 STATES OF TITANIUM

State	θ	*R.E.* (eV) in $TiCl_4$	*V* (eV)	Sh_1	Sh_2
d^4, C_{4v}	113°	1·11	4·52	2·108	
d^3s, C_{3v}	90°	0·06	1·83*	1·000	2·226
T_d	{ 54°44′	0·00	2·00	2·437*	2·437*
	{125°16′				
d^2p, C_{2v}	148°25′	664	4·41*	1·732	2·076
	135°33′	1·55	5·46	2·803*	2·706*
	108°26′	0·00*	5·08	2·236	1·739
d^2sp, C_{2v}	130°48′	0·48	2·91*	2·000*	2·634*
	108°26′	0·00*	3·10	1·000	1·739
d^2p^2, $(zx\sigma\pi)D_{4h}$	{ 45°, 135°,	0·28	8·03	2·473	
	{225°, 315°,				
$(zx\sigma\partial)D_{4h}$	{ 0°, 90°,	0·28	7·37	2·806	2·594
	{180°, 270°				
dsp^2, D_{4h}	90°	0·28	7·20*	1·932	2·594
		0·28	7·39	2·693*	2·693*
dp^2, C_{2v}	125°15′	0·25*	11·54	2·236	1·732
	156°15′	1279	12·12	2·806*	1·906*
sp^3, T_d		0·00	12·64	2·000	2·000

* States are marked thus in the same manner as for Table 3.

compounds, and in fact, the $TiCl_4$ molecule has been found to have the tetrahedral structure.[20] Other configurations than d^3s, having superior bonding-power, are disadvantageous from the viewpoints of steric repulsion, or excitation energy, or both. The configuration sp^3, T_d, compares unfavourably in bonding-power, and in excitation energy, with d^3s: but again, it appears that a hybrid, obtained by mixing

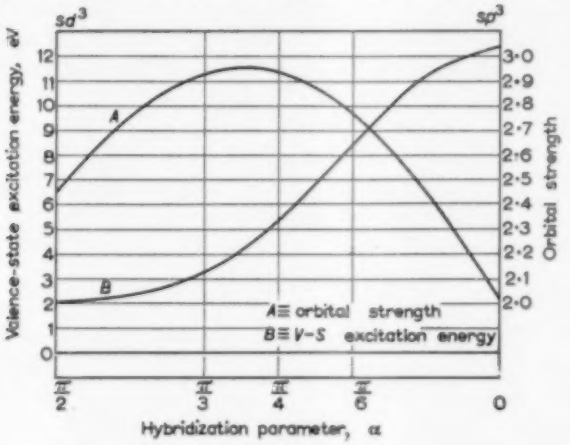

FIG. 2

d^3s with sp^3, has the advantage over both parents. The regular tetrahedral orbitals deriving from $sd^{3-n}p^n$ (where $0 \leqslant n \leqslant 3$) may be written:—

$$h_1 = \tfrac{1}{2}(s + \cos\alpha\,(x + y + z) + \sin\alpha\,(\pi + \pi' + \partial'))$$

$$h_2 = \tfrac{1}{2}(s + \cos\alpha\,(-x + y - z) + \sin\alpha\,(\pi - \pi' - \partial'))$$

etc.

and have maximum strength, $S = 2{\cdot}945$, when $\tan\alpha = \sqrt{5/3}$. They have been given previously, in somewhat different forms, by KUHN.[25] Fig. 2 shows how the excitation energy and orbital strength vary with the mixing parameter α. The maximum orbital strength, $S = 2{\cdot}945$, derives from the configuration $sp^{9/8}d^{15/8}$, which requires an excitation energy of 4·17 eV. As in the case of pentavalent vanadium, it would appear most profitable to adopt a *little* isovalent hybridization: thus, S increases from 2·44 for the pure sd^3 configuration, to $>2{\cdot}9$ very rapidly on admixture of a little sp^3, for an additional cost of less than 1 eV.

The configuration giving rise to the "strongest" set of square planar orbitals (symmetry D_{4h}) is an isovalent hybrid built up from dsp^2 and d^2p^2, and has been described previously by KUHN.[25] The maximum strength, $S = 2{\cdot}943$, is slightly less than given by the strongest tetrahedral bonds. The excitation energy to achieve square bonds of maximum strength in titanium is calculated to be 7·32 eV—i.e. ca. 3 eV more than required to achieve tetrahedral bonds of similar strength. Since the steric repulsion factor is also less favourable for the square structure, the tetrahedron is superior in every way. We have not attempted to construct the strongest set of pyramidal orbitals (C_{3v}), as this structure is sterically unfavourable over a wide range of the angle θ.

The pentachloride VCl_5 has not been prepared, but the tetrachloride VCl_4 is

[25] H. KUHN, *J. chem. Phys.* **16**, 727 (1948).

known, and has been shown to have the tetrahedral structure.[22] The valence-state of V in VCl_4 may be represented $\sigma h_1 h_2 h_3 h_4$, where h_{1-4} are the generalized tetrahedral bonding orbitals already described in discussing $TiCl_4$. Using parameter values from Table 2, the valence-state energy for V in VCl_4 is (in cm^{-1}), 146344–211084 $\sin^2 \alpha +$ 83990 $\sin^4 \alpha$, from which it follows that bonds of strength $S > 2{\cdot}9$ are available for an excitation energy of ca. 4 eV. Referring back to Fig. 1, we may note that in order to form bonds of similar strength ($S > 2{\cdot}9$) in the trigonal bipyramid VCl_5, an excitation energy of ca. 7 or 8 eV is required. Hence, the formation of VCl_5 from VCl_4 is faced by an increase in the valence-state energy barrier of ca. 3 eV, which, coupled with the increased steric repulsion in the trigonal bipyramid, could account for the difficulty of preparing VCl_5, and its instability relative to VCl_4.

Values are given in Table 5 of the heats of formation (ΔH_f°) of gaseous[26] $TiCl_4$, $TiCl_3$, and $TiCl_2$, the heats of atomization[27,28] to ground-state atoms (H_a), and the bond-energy term values, E(Ti–Cl), obtained by dividing H_a by the number of Ti–Cl bonds.

TABLE 5

Compound	ΔH_f° (kcal/mole)	H_a (kcal)	E(Ti–Cl)
$TiCl_4$	−181·6	410·2	102·5
$TiCl_3$	−128·7	328·3	109·4
$TiCl_2$	−69·4	240·0	120·0

From these data, the following dissociation energies are derived:

$D(Cl - TiCl_3) = D_1 = 81{\cdot}9$ kcal/mole; $D(Cl - TiCl_2) = D_2 = 88{\cdot}3$ kcal/mole; and the sum, $D(Cl - TiCl) + D(Ti - Cl) = D_3 + D_4 = 240{\cdot}0$ kcal/mole. Hence, $(D_3 + D_4) > (D_1 + D_2)$ by ca. 70 kcal/mole. A similar situation is found in other tetrahalides: for example, from the heats of formation[29] of gaseous $SnCl_4$ (−120·7 kcal/mole), and of $SnCl_2$(−54·7 kcal/mole), and the heat of atomization of tin,[30] it follows that $(D_3 + D_4) > (D_1 + D_2)$ in $SnCl_4$ by ca. 59 kcal/mole. The equilibrium measurements on the system $SiCl_4 + Si \rightleftharpoons 2\ SiCl_2$ by SCHÄFER and NICKL,[31] in conjunction with the heat of formation of gaseous $SiCl_4$ and the heat of atomization of silicon,[32] indicate that $(D_3 + D_4) > (D_1 + D_2)$ by ca. 22 kcal/mole in $SiCl_4$.

Variable dissociation energies in the stepwise disruption of MX_n molecules have been remarked upon previously,[33] and discussed in relation to the energies of excitation of atoms from their ground-states to higher valencies. The stepwise dissociation of $TiCl_4$ presents an interesting case for discussion, but in the absence of knowledge of the geometrical structures of gaseous $TiCl_3$ and $TiCl_2$, discussion must be somewhat tentative.

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We assume a trigonal planar structure for $TiCl_3$. The three bonding orbitals, h_1, h_2, h_3, are the same as the trigonally disposed radial bonds ($h_{3,4,5}$) of the trigonal bipyramid. The free electron in $TiCl_3$ may be placed in any one of six orbitals orthogonal to the bonding orbitals, but the orbital $h_4 = [(\cos\alpha)s + (\sin\alpha)\sigma]$ is to be

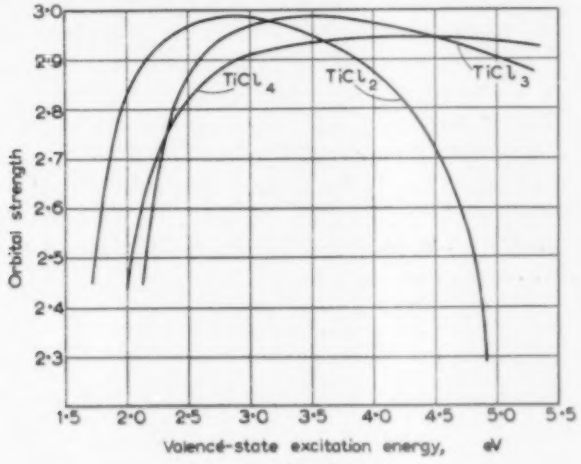

FIG. 3

preferred if one seeks the configuration of minimum excitation energy. The orbital strengths, for different values of α and β, have been given previously: the calculated valence-state excitation energies, placing the free electron in h_4, are listed below (values in eV):

α \ β	0	$\pi/6$	$\pi/4$	$\pi/3$	$\pi/2$
0	1·83	2·59	3·75	5·32	7·30
$\pi/6$	1·99	2·67	3·76	5·24	7·17
41°48′	2·07	2·70	3·74	5·18	7·03
$\pi/4$	2·09	2·70	3·72	5·14	6·98
$\pi/3$	2·12	2·65	3·60	4·96	6·73
$\pi/2$	2·09	2·55	3·43	4·83	6·41

In Fig. 3, the orbital strength S is plotted against the excitation energy for the particular choice $\alpha = 41°48'$ (which leads to bonds of maximum strength). On the same graph, the corresponding curve for the tetrahedral orbitals of Ti (as in $TiCl_4$) is plotted. The figure shows clearly the superior bonding power of the trigonal orbitals in the regions where $S > 2{\cdot}9$; moreover these strong bonds are less costly to achieve in $TiCl_3$ than in $TiCl_4$.

We assume an angular model for $TiCl_2$, with the $\overline{/Cl—Ti—Cl} \sim 120°$. The bonding orbitals, h_1, h_2, are again the trigonal orbitals, as in $TiCl_3$. We have considered a triplet state, in which the two free electrons are placed with parallel spins in the orthogonal orbitals, $h_3 = [(\cos\alpha)s + (\sin\alpha)\sigma]$, and $h_4 = \pi$, and a singlet state in which the non-bonding electrons are placed with opposite spins in h_3. The

valence-state excitation energies of both the triplet and singlet states were calculated, and are of similar magnitude in the region where $S > 2{\cdot}95$: of the two, however, the singlet is slightly the more economical. The plot of orbital strength against excitation energy for the singlet state is included in Fig. 3. It is apparent that strong bonds ($S > 2{\cdot}9$) are more easily attained in $TiCl_2$ than in $TiCl_3$.

We assume that the bonding orbital in TiCl is of the trigonal type. The uncoupled electrons are placed in the orbitals $h_2 = [(\cos\alpha)s + (\sin\alpha)\sigma], h_3 = \pi, h_4 = \pi'$, in the quartet state, and in h_2 (paired) and h_3 in the doublet state. The calculated valence-state energies for both states are closely similar, particularly in the range of α, β corresponding to formation of a strong bonding orbital.

The following table lists the excitation energies required to form bonding orbitals of *maximum* strength in $TiCl_4$, $TiCl_3$, $TiCl_2$ and TiCl, and also gives the calculated ionization potentials of a *bonding* electron of Ti in these configurations.

Compound	Isovalent configuration	S	*V.E.* (eV)	*I.P.* (eV)
$TiCl_4$	$sp^{9/5}d^{15/5}$	2·945	4·17	9·26
$TiCl_3$	$sp^{8/5}d^{19/5}$	2·987	3·47	8·42
$TiCl_2$				
singlet	$s^{35/27}p^{16/27}d^{8}$	2·987	2·92	8·05
triplet	$s^{35/27}p^{16/27}d^{35/9}$	2·987	3·07	6·69
TiCl				
doublet	$s^{54/27}p^{8/27}d^{22/6}$	2·987	2·80	6·87
quartet	$s^{19/27}p^{8/27}d^{2}$	2·987	2·66	4·83

As already pointed out, it may be profitable, in practice, for the titanium atom to adopt orbitals of less than maximum strength: furthermore, the structural models we have assumed may well be unrealistic. Hence, we cannot attach more than qualitative significance to this table. The features of importance are that the excitation energy to the valence-state probably decreases in the sense $TiCl_4 > TiCl_3 > TiCl_2 \sim$ TiCl, and that the electronegativity of the Ti atom (as reflected by the valence-state ionization potentials) may decrease in similar manner. The reason for these variations is that the degree of *p*-character in the isovalent configurations required to produce 4, 3, 2, and finally only one *strong* bonding orbital, decreases with the number of bonding orbitals.

The question posed by Table 5 is to explain the increase in E (Ti—Cl) in passing from $TiCl_4 \rightarrow TiCl_2$. Both the features mentioned above, of diminishing excitation energy, and of increasing ionic character, operate qualitatively in influencing the bond-strengths in the observed direction.

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TETRAVALENT AMERICIUM AND CURIUM; THE ABSORPTION SPECTRA OF THE TRI- AND TETRAFLUORIDES OF THESE ELEMENTS*

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(*Received* 15 *January* 1958)

Abstract—A technique has been developed for spectral examination of sub-milligramme amounts of solid compounds. The absorption spectra of curium(IV) fluoride and americium(IV) fluoride have been measured. A Cary Model 14M Recording Spectrophotometer was used to record the spectra over the region 3500–20,000 Å.

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TETRAVALENT americium and curium have been prepared only in the solid dioxides[1,2] and tetrafluorides.[3,4] No evidence of tetravalency in aqueous solution has been reported, the trivalent being the stable state for both elements.[5] This paper reports the absorption spectra of both tetravalent americium and curium as tetrafluorides over the region 3500–20,000 Å. The absorption spectra of americium and curium trifluorides are included for comparison. The recently discovered absorption at about 4000 Å in aqueous curium(III)[6] is well confirmed in the solid trifluoride.

Previously, the absorption spectra of solid CmF_3,[7] and GdF_3[7] and UF_4[8] were measured using a spectrographic technique. Visual observations were made of the absorption of AmF_3,[7,9] AmF_4,[7,9] CmF_3,[9] CmF_4,[4] GdF_3,[7] TbF_3[7] and TbF_4.[7] Only AmF_3, AmF_4, and CmF_4 gave discernible absorption in the visible region. There has apparently been no investigation at wavelengths longer than 7000 Å.

EXPERIMENTAL

The americium-241 and curium-244 used for these measurements were carefully purified in this laboratory and contained no impurities detectable by spectroscopic analysis. Quick removal of americium from curium was accomplished by a novel method which involved ozone oxidation of the americium to the soluble (VI) state from a slurry of mixed Am(III) and Cm(III) hydroxides in in ca. 0·3 M $NaHCO_3$.[10] The Cm(III) hydroxide is unchanged by this treatment. All chemicals were of Analytical Reagent grade and were used without further purification. Fluorine gas was obtained from pressurized cylinders and was purified by passing it through a sodium fluoride trap to remove hydrofluoric acid.

Containers for the spectral examination of the solid fluorides were made from crystalline optical quality calcium fluoride disks $\frac{1}{2}$ in. diameter × $\frac{1}{2}$ in. thick. A $\frac{1}{2}$ in. dia. flat-bottomed well was ground into a disk to a depth of about $\frac{3}{16}$ in. By trial, it was found that 0·5 mg of either americium or curium fluoride spread over the bottom of this well gave a good absorption spectrum.

* This work was sponsored by the U.S. Atomic Energy Commission.

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(3) L. B. ASPREY, *J. Amer. chem. Soc.* **76**, 2019 (1954).
(4) L. B. ASPREY, F. H. ELLINGER, S. FRIED and W. H. ZACHARIASEN, *J. Amer. chem. Soc.* **79**, 5825 (1957).
(5) Ref. 1, pp. 508 and 526.
(6) W. T. CARNALL, P. R. FIELDS, D. C. STEWART and T. K. KEENAN, *J. inorg. nucl. Chem.* **6**, 213 (1958).
(7) D. C. FEAY, *UCRL*–2547 (1954), University of California Thesis.
(8) D. M. GRUEN and M. FRED, *J. Amer. chem. Soc.* **76**, 3850 (1954).
(9) E. STARITSKY, Los Alamos Scientific Laboratory, Private communication.
(10) J. S. COLEMAN and T. K. KEENAN, Los Alamos Scientific Laboratory, Unpublished work.

Due to the intense α-activity of these elements, the following operations had to be carried out in a glove box. The 0·5 mg of the particular element in a volume of 10 μl was introduced into the depression in the calcium fluoride disk. An equal volume of concentrated hydrofluoric acid was added and the resulting slurry was stirred with a platinum rod to give a uniform deposit of the trifluoride. The precipitate was then dried in air on a hot plate by slowly increasing the temperature to 200°. Usually some cracking or shrinking of the precipitate occurred and it was necessary to slurry with water and redry. Such a preparation was used directly to obtain the spectral data on the trifluoride compounds and as a starting material for the preparation of the tetrafluoride compounds.

Oxidation of the trifluoride compound was carried out in a nickel fluorinator previously described.[3] The calcium fluoride disk containing the trivalent salt was treated with one atmosphere of fluorine at a temperature of 400° for 1 hr. Complete oxidation of either americium or curium

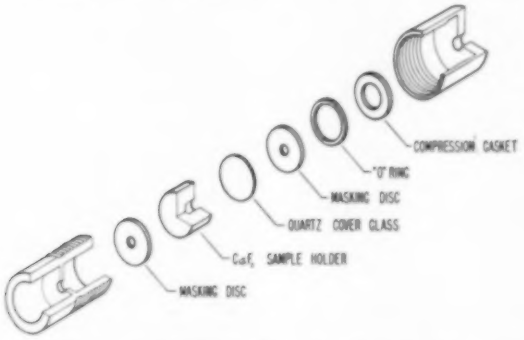

FIG. 1.—Sample holder for radioactive materials.

to the (IV) state was accomplished under these conditions. However, it was found that the quality of the spectra of the tetravalent compounds gradually deteriorated with time, some growth of characteristic trivalent absorption being noted. The tetravalent fluoride spectra reported in this paper were recorded as soon as possible after fluorination to eliminate any error caused by this effect. No peaks at the (III) positions were observed under these conditions. This was taken as adequate proof of complete oxidation to the (IV) state.

For spectral examination, the well in the disks which held the sample was covered with a 1 mm quartz cover glass which was fastened in place by a thin layer of fluorocarbon grease. This assembly was placed in a brass holder which incorporated appropriate columnating masks to restrict the light path so that it passed only through the sample. Fig. 1 is a drawing of the optical assembly. The brass holder was of such dimensions as to fit the sample carriage of the spectrophotometer.

A Model 14M Cary Recording Spectrophotometer was used for the spectral measurements. A constant temperature of 25° was maintained in the cell compartment. Appropriate equipment was not available for spectral studies at low temperatures although better resolution of the peaks would doubtless be obtained at these conditions. The instrument was operated at maximum sensitivity because of the relative opacity of the samples. The amount of light passing through the reference compartment of the double-pass spectrophotometer was reduced by means of aluminium columnating disks. In general, a hole of 0·020 in. was used as a reference for the fluoride samples and allowed adequate balancing of the instrument. In some cases, thin disks of ThF_4–KBr were used as the reference.

A few trials were carried out by using a slurry of the fluoride in oil of the appropriate refractive index. The results using this latter technique were not as satisfactory as those obtained with the fluorides in the dry state.

RESULTS AND DISCUSSION

Typical results are presented in Figs. 2–5 covering the region 3500–20,000 Å. Because of the attenuation of the light by the translucent sample, the actual optical densities are about 5·0–8·0. Although many attempts were made to examine the

ultra-violet spectra, it was not possible to detect discrete maxima below 3500 Å. The strong general ultra-violet absorption characteristic of all these compounds prohibited any systematic examination of this region. Some irregularities were observed in almost every case, but were considered too weak for reliable evaluation.

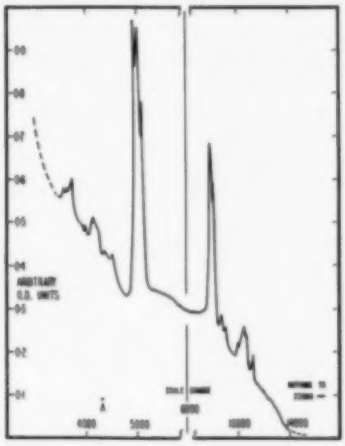

FIG. 2.—Spectrum of trivalent americium fluoride.

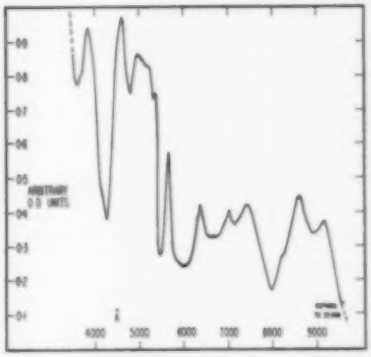

FIG. 3.—Spectrum of tetravalent americium fluoride.

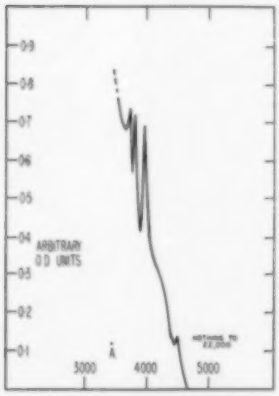

FIG. 4.—Spectrum of trivalent curium fluoride.

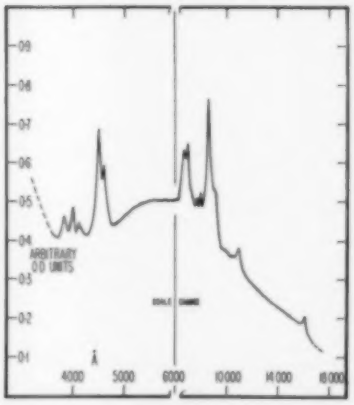

FIG. 5.—Spectrum of tetravalent curium fluoride.

Table 1 lists the positions and the relative intensities of the observed maxima. It was impossible to estimate specific absorption constants because of the unknown thickness of the samples. We believe the reliability of the positions of the sharp or moderate peaks (those marked *s* or *m* in the tables) to be accurate to ± 10 Å and the weak peaks (those marked *w*) to be accurate to ± 25 Å.

The agreement of the trivalent fluoride spectra with those of the corresponding trivalent ions is very close. For example, the aqueous spectra of trivalent americium and curium are shown in Figs. 6 and 7 and may be compared with Figs. 2 and 4. It is interesting to note that in the fluoride spectrum, the strong 5027 Å aqueous maximum

of trivalent americium is resolved into three distinct components. In general, the prominent peaks in the trifluoride spectra occur at wavelengths some 20–30 Å shorter than those in the aqueous system.

Most of the previous estimates of absorption in the tetravalent compounds (based on visual observation) are confirmed with regard to the positions of the "strong" maxima of the present work. However, the excellent resolution of the Cary instrument allowed more definite assignment of the wavelength of these peaks. In addition, a

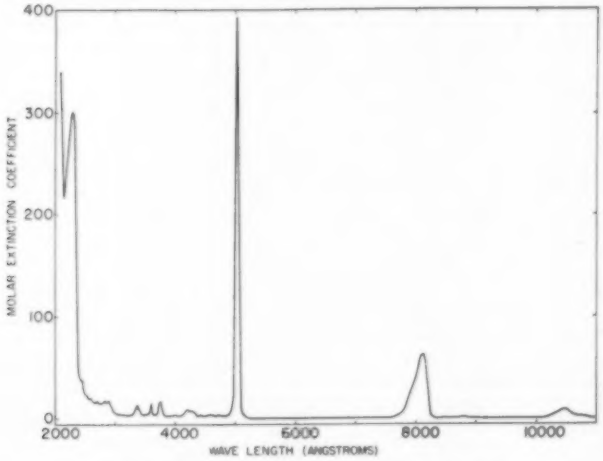

FIG. 6.—Spectrum of aqueous trivalent americium.

TABLE 1.—ABSORPTION MAXIMA (ÅNGSTROMS) OF TRI- AND TETRAFLUORIDES OF AMERICIUM AND CURIUM

AmF_3	CmF_3	AmF_4	CmF_4
3600 *w*	3740 *m*	3760 *s*	3865 *m*
3652 *w*	3780 *m*	4530 *s*	4010 *m*
3760 *m*	3950 *s*	4860 *w*	4118 *m*
4003 *w*	4490 *w*	5360 *w*	4504 *s*
4150 *w*		5680 *s*	4607 *m*
4378 *w*		6390 *m*	6730 *w*
4530 *w*		7030 *m*	6960 *w*
5006 *s*		7440 *m*	7650 *w*
5085 *s*		8620 *m*	7915 *w*
5148 *m*		9180 *m*	8560 *s*
7900 *s*			9100 *w*
8250 *w*			10975 *w*
9015 *w*			16120 *w*
9918 *w*			
10460 *m*			
10660 *w*			
11120 *w*			

s = sharp peak *m* = moderately sharp peak *w* = weak or very broad peak.

number of weaker maxima were found and the spectral region examined was extended down to 3500 Å and also out to 20,000 Å.

Absorption in $4f^7$ Gd(III) is confined to the region <3200 Å.[11] The electronic transitions of $5f^7$ Cm(III) lie at lower energies since the absorption bands are moved

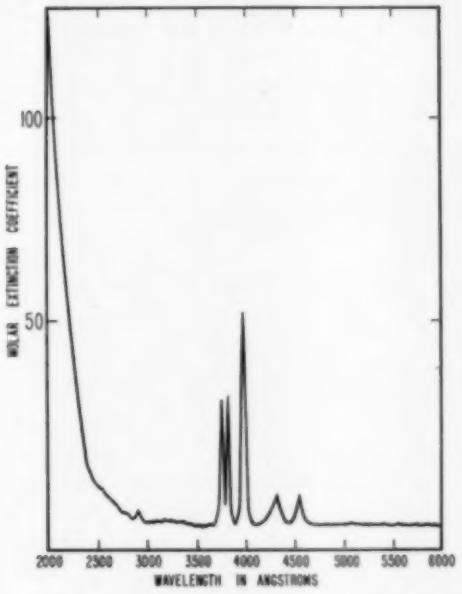

FIG. 7.—Spectrum of aqueous trivalent curium.

further toward the visible.[6] This fact and the existence of Cm(IV) is further evidence that the 5*f* electrons in the actinide elements are less tightly bound than the corresponding 4*f* electrons in the lanthanides.

[11] T. MOELLER and F. A. J. MOSS, *J. Amer. chem. Soc.* **73**, 3149 (1951).

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INFRA-RED SPECTRA OF TRANSITION METAL–NITRIC OXIDE COMPLEXES—I

COMPLEXES INVOLVING DONATION FROM THE NO^+ ION

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(*Received* 7 *February* 1958)

Abstract—Infra-red spectra of numerous transition metal–nitric oxide complexes have been measured and an attempt has been made to correlate the position of N—O stretching frequencies with the nature of the binding of the nitric oxide group in the complexes.

ALTHOUGH there have been several reports[1–10] concerning the infra-red spectra of certain transition metal–nitric oxide complexes of various types, there is so far no survey of the spectra of known compounds sufficiently general to allow conclusions to be made concerning the nature of the binding of the NO group in such complexes. Accordingly, in the present and the following paper, previous measurements and new data are collected on most types of nitric oxide complexes known at present and which are sufficiently stable to allow their spectra to be obtained.

The status of the chemistry of the nitric oxide group has been recently reviewed[11] and excellent accounts are given elsewhere.[12] Briefly, we may note firstly that nitric oxide compounds of transition metals may be either cationic, anionic or neutral, depending on the nature and valence state of the metal and on the type of other ligands present. Secondly, we may note that in principle nitric oxide can combine with a transition metal in the following ways:

(a) by donation of two electrons from neutral NO to give paramagnetic complexes $M \leftarrow \dot{N}{=}O$. There is very little evidence for the existence of metal complexes involving this type of bonding.

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[1] D. P. MELLOR and D. P. CRAIG, *Proc. roy. Soc. N.S.W.* **78**, 25 (1944).
[2] L. N. SHORT, *Rev. pure appl. Chem.* **4**, 41 (1954).
[3] F. A. MILLER and C. H. WILKINS, *Analyt. Chem.* **24**, 1253 (1952).
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[5] J. M. FLETCHER, I. L. JENKINS, F. M. LEVER, F. S. MARTIN, A. R. POWELL and R. TODD, *J. inorg. nucl. Chem.* **1**, 378 (1955).
[6] T. S. PIPER, F. A. COTTON and G. WILKINSON, *J. inorg. nucl. Chem.* **1**, 165 (1955).
[7] T. S. PIPER and G. WILKINSON, *J. inorg. nucl. Chem.* **3**, 104 (1956).
[8] T. S. PIPER and G. WILKINSON, *J. Amer. chem. Soc.* **78**, 900 (1956).
[9] T. S. PIPER and G. WILKINSON, *J. inorg. nucl. Chem.* **2**, 38 (1956).
[10] J. CHATT, L. A. DUNCANSON and L. M. VENANZI, *Suomen. Kem.* B **29**, 75 (1956).
[11] C. C. ADDISON and J. LEWIS, *Quart. Rev.* **IX**, 115 (1955).
[12] T. MOELLER, *Inorganic Chemistry* p. 595. Wiley, New York (1952); N. V. SIDGWICK, *Chemical Elements and their Compounds*. Oxford (1950).

(b) by donation as in (a) but with coupling of the unpaired electron on the NO group with an unpaired *d* electron of the metal to give a π–bond. An alternative way of regarding this type of bond is to consider a one-electron transfer from NO to the metal followed by donation of two electrons from the NO^+ ion. We have in this case the canonical forms

$$M^- \leftarrow N^+ \equiv O \rightleftarrows M = N = O.$$

The majority of metal complexes cited in this paper can be formulated with this type of M—NO bond.

(c) by transfer of an electron from the metal to NO and donation of two electrons from the NO^- ion. This type of bonding occurs in a few cobalt complexes and will be discussed in a following paper.

(d) the NO group is not bonded to the metal in an "end-on" position with a linear M—N—O group, but is bonded at some angle; the π-electrons of the multiple bond in NO may be regarded as to some extent taking part in the bonding in a manner similar to the case of ethylenic bonds in the well known transition metal–olefin complexes. Evidence for this type of bonding has only recently been obtained.[13] The bond is closely related to type (b) above and may occur in several of the complexes noted in this paper.

(e) the NO group is bonded in a bridging position >N=O in a manner similar to the bonding of carbon monoxide in certain polynuclear carbonyls. Only one example of this type of bonding for NO seems to have been established.[9]

The infra-red spectra of the complexes given in Tables 1–3 can all be considered to be derived from nitric oxide bonding in the ways (b) and (d) above.

DISCUSSION

The N—O stretching frequencies of Tables 1–3 and of Table 3 in the following paper cover a greater range than has been observed for C—O stretching frequencies in metal–carbon monoxide compounds. In the nitrosyls, the range is from ~1940 cm^{-1} to 1045 cm^{-1}, whereas in the carbonyls it is from ~2100 cm^{-1} to ~1850 cm^{-1}. Since the complexes discussed here can all be formulated with donation from the NO^+ ion, it is pertinent first to note that the change in the N—O stretching frequency from nitric oxide to the nitrosonium ion is from 1878 cm^{-1} in NO[14] to ~2220 cm^{-1} in various nitrosonium salts.[15] This change is consistent with the removal of an electron from an anti-bonding orbital in nitric oxide and a concomitant increase in the bond strength of the N—O bond in the ion.[16] The co-ordination of the NO^+ ion to a metal atom would be expected to lead to a further decrease in the N—O stretching frequency; the frequencies observed in the complexes appear to lie in the range 1938 cm^{-1}, in the nitroprusside ion $[NOFe(CN)_5]^{2-}$, to 1626 cm^{-1} in the compound $NOCo[(CH_3)_2NCS_2]_2$.

Of all the transition metals, ruthenium, as is well known, forms an unusually large number of nitric oxide complexes, many of which have remarkable stability. It is noteworthy that in most of these ruthenium complexes, the metal atom is in

[13] P. R. H. Alderman and P. G. Owston, *Nature, Lond.* **178**, 1071 (1956).
[14] E. L. Saier and A. Pozefsky, *Analyt. Chem.* **26**, 1079 (1954).
[15] D. J. Millen and D. Watson, *J. chem. Soc.* 1369 (1957).
[16] cf. C. A. Coulson, *Valence* p. 152. Oxford (1952).

TABLE 1.—NEUTRAL COMPLEXES AND NITROSYL HALIDES

Compound	N—O stretch (cm^{-1})	State	Reference (* signifies present measurement)
$(NO)_2CrC_5H_5Cl$	1818(s) 1711(s)	solution	6
$(NO)_2CrC_5H_5Br$	1820(s) 1717(s)	solution	6
$(NO)_2CrC_5H_5SCN$	1824(s) 1722(s)	solution	6
$(NO)_2CrC_5H_5CH_3$	1779(s) 1670(s)	solution	4
$(NO)_2CrC_5H_5C_2H_5$	1777(s) 1673(s)	solution	4
$(NO)_2CrC_5H_5\sigma C_5H_5$	1787(s) 1685(s)	solution	4
$(NO)_2CrC_5H_5CH_2Cl$	1797(s) 1704(s)	solution	4
$(NO)_2CrC_5H_5C_6H_5$	1790(s) 1685(s)	solution	4
$NOMo(CO)_2C_5H_5$	1678(s)	solution	4
$(NO)_2Mn_2(C_5H_5)_2$	1731(s)	solution	6
	1510(s) (bridging NO)		
$NOMn_2S_2C_5H_5$	1743(s)	KBr disc	5
$[(NO)_2Fe(SC_2H_5)]_2$	1764(s) 1744(s)	mull	*
$[(NO)_2FeI]_n$	1795(s) 1760(s)	mull	*
$(NO)_2Fe[P(C_6H_5)_3]_2$	1715(s) 1669(s)	solution	*
$[NOFe(Et_2NCS_2)_2]$	1673(s)	mull	*
$NORu(OH)_3$	1847(s)	mull	*
$NORu(Me_2NCS_2)_2$	1845(s)	mull	*
$NORuCl_5 \cdot 3H_2O$	1895(s, very broad)	mull	*
	1800		
$NORuCl_2$ *o*-phen.	1881(s)	mull	*
	1896(sh)		
$NOCo(Me_2NCS_2)_2$	1626	mull	3
$(NO)_2CoI$	1880(s) 1817(s)	mull	*
	1800		
$NOCo(CO)_4$	1832(s)	gas	*
$(NO)_2CoI$ *o*-phen.	1775(s)	mull	*
$NOCo(CO)P(C_6H_5)_3$	1754(s)	solution	*
	2012(s) (CO)		
$NOCo(CO)_2[P(OC_6H_5)_3]_2$	1754(s)	solution	*
	2053(s) 1988(s) (CO)		
$NOCo(CO)_2Sb(C_7H_7)_2$	1762(s)	solution	*
	2043(s) 1988(s) (CO)		
$NOCo(CO)_2As(C_7H_7)_2$	1754(s)	solution	*
	2049(s) 1888(s) (CO)		
$[NONiSC_6H_5]_n$	1785(s)	KBr disc	*
$[NONiSC_2H_5]_n$	1760(s)	KBr disc	*
$NONiC_5H_5$	1820(s)	solution	12

the +3 oxidation state, and a plausible explanation of the unique nature of ruthenium–nitric oxide chemistry is that the combination of nitric oxide with +3 ruthenium in an octahedral complex would lead to an inert gas configuration for the metal atom. At the same time, this would allow the maximum amount of π-bonding between the metal and nitrogen atoms from the three filled lower *d* orbitals. On this view, a similar stability of the M—NO group might have been expected with iron and osmium. This is not the case with +3 iron, where nitric oxide complexes are not

TABLE 2.—ANIONIC COMPLEXES

Compound	N—O stretch (cm^{-1})	State	Reference (* signifies present measurement)
$[NOMn(CN)_5]K_2$	1730(s) (broad)	mull	*
$[(NO)_2FeS]K$ (red salt)	1716(s) (broad)	mull	*
$[(NO)_7Fe_4S_3]K \cdot H_2O$ (black salt)	1716(s) (v. broad) 1598	mull	*
$[NOFe(CN)_5]Na_2$	1925(s)	KCl disc	2
	1938(s)	KBr disc	7
$[NOFe(CN)_5]K_2H_2O$	1937(s)	mull	*
$[(NO)_2Fe(S_2O_3)]K_2 \cdot H_2O$	1801(s) 1734(s)	mull	*
$[NORuOH(NO_2)_4]K_2$	1900(s)	mull	*
$[NORuOH(NO_2)_4]Na_2 \cdot 2H_2O$	1907(s)	KBr disc	*
$[NORuCl_5]Na_2 \cdot H_2O$	1911(s)	mull	*
$[NORuCl_5]K_2$	1905(s)	mull	*
$[NORuCl_5]Cs_2$	1880(s)	mull	*
$[NORuI_5]K_2$	1850(s) (broad)	mull	*
$[NORu(CN)_5]K_2$	1930(s) (broad)	mull	*
$[NOOsOH(NO_2)_4]K_2$	1893(s)	mull	*
$[(NO)_2Co(S_2O_3)_2]K_2$	1720(s) (broad)	mull	*
$[NONi(S_2O_3)_2]K_2 \cdot 2H_2O$	1759(s)	mull	*
$[NOPtCl_5]K_2$	1711(s)	mull	*

TABLE 3.—CATIONIC COMPLEXES

Compound	N—O stretch (cm^{-1})	State	Reference (* signifies present measurement)
$[NOMn(CO)_2C_5H_5]_2PtCl_6$	1850 (s)	KBr disc	12
$[NORuOH(NH_3)_4]Cl_2$	1845 (s)	KBr disc	*
$[NORuCl(NH_3)_4]Cl_2$	1894 (s)	KBr disc	*
$[NORuBr(NH_3)_4]Br_2$	1885 (s)	KBr disc	*

readily formed and where they do exist they are of much lower stability than the ruthenium analogues. This difference may be attributed to the fact that the majority of ferric complexes are of the outer orbital type, due to the stability of the half-filled 3*d* shell in the ferric ion. Only where monodentate ligands, like cyanide, which have a very strong ligand field effect, are present, and the complexes are of the inner orbital type, are nitric oxide complexes of +3 iron stable. In the case of osmium, the +3 oxidation state is relatively unstable and the number and stability of osmium–nitric oxide complexes is much lower than for ruthenium.

Considering the infra-red spectra of the ruthenium complexes, it may be noted that the frequencies are all relatively high and show rather a small range, lying

between 1845 cm^{-1} in $NORu[(CH_3)_2NCS_2]_2$ and 1930 cm^{-1} in $[NORu(CN)_5]K_2$. That these frequencies are not inconsistent with a formulation involving considerable multiple bonding between ruthenium and nitrogen, i.e., Ru=N, is indicated by comparing them with the frequencies of carbon monoxide in its complexes where substantial multiple bonding between the metal and carbon atom is generally accepted. The N—O frequency in the nitroprusside ion $[NOFe(CN)_5]^{2-}$ is among the highest observed; from a consideration of the position and the band width of the C—N stretching frequencies in the ferrous and ferric substituted cyano complexes, HERINGTON and KYNASTON[4] concluded that there was a high degree of multiple bonding between the metal and nitrogen atoms in the nitroprusside. The reduction in the N—O stretching frequencies that occurs in several compounds of the first transitional series elements below the lowest values for ruthenium compounds cannot be attributed to the lighter mass of these atoms as this would have been expected to lead to a higher or at least comparable value for the frequency and hence the reduction may be attributed to either or both of two effects. Firstly, for all complexes except $K_2[NOPtCl_5]$ and $K_3[NOMn(CN)_5]$, the stereochemistry involves either a tetrahedral or a tetragonal pyramidal arrangement of bonds; for both these configurations the possible π-bonding is greater than in the octahedral case[17] for ligands of the same type. Secondly, the nitric oxide group may be bound in an asymmetric manner to the metal atom as has been observed in $NOCo[(CH_3)_2NCS_2]_2$.[11] It may be noted here that a recent microwave study of C_5H_5NiNO[18] shows that the Ni—N—O group is linear with a computed Ni—N distance of 1·68 Å; this implies considerable multiple bond character in the Ni—N bond consistent with the observed frequency of 1820 cm^{-1}.

A further point obtained from a consideration of the frequencies in the ruthenium complexes is that there is no significant difference between the N—O frequencies in cationic and in anionic complexes. A difference would certainly have been expected if the nitric oxide were bound differently in the two cases, i.e., the nitric oxide groups could be regarded as NO^+ and NO^-, as has been suggested previously.[1]

For a given metal, substitution of ligands with differing electronegativity might have been expected to give rise to changes in the N—O frequencies by inductive effects, and some small changes have been observed. However, since the compounds were studied in the crystalline state such changes are of doubtful significance, and it may be noted that in the cases of the compounds $(NO)_2CrC_5H_5R$, which were studied in solution, only very small changes depending on the electronegativity of R were observed.

In the compounds where two nitric oxide groups are present, two N—O frequencies are always observed consistent with a *cis* configuration of the groups, except in the case of $[(NO)_2CoI]_n$ where three sharp bands were found—this splitting may well arise from local asymmetry in the crystal. The compound reported in the literature as $K_2[Os(NO_2)_5]$ was found to be diamagnetic and was observed to have an N—O frequency at 1893 cm^{-1}. The compound must hence be formulated similarly to the corresponding ruthenium compound,[5] i.e. as $K_2[NOOs(NO_2)_4OH]$.

In the compound $(C_5H_5)_3Mn_2(NO)_3$, the N—O stretching frequency at 1510 cm^{-1} was assigned to a bridging NO group;[9] it is interesting to note that in the recently

[17] G. GIACOMETTI, *J. chem. Phys.* **23**, 2068 (1955).
[18] A. P. COX, L. F. THOMAS and J. SHERIDAN, Birmingham University. Private communication.

determined structure of Roussin's black salt[19] one of the NO groups is considered to differ from the other six, involving a shorter metal-nitrogen distance and a lower bond-order for the NO group. Consistent with this we find broad non-resolvable absorption in the 1710 cm^{-1} region with a well defined shoulder at 1598 cm^{-1}, the latter perhaps being associated with the anomalous apex NO group which would have a bond-order similar to that of the bridging NO group referred to above.

EXPERIMENTAL

The compounds studied were all prepared by methods given in the literature, with the exception of the compounds whose preparation is given below. We are indebted to PROFESSOR MALATESTA for his kind gift of substituted phosphine carbonyl nitrosyls. The spectra were taken in CS_2 and CCl_4 where possible and otherwise in halide discs or nujol mulls. Measurements were made with a Perkin–Elmer Model 21 and Grubb–Parsons double-beam instruments using sodium chloride optics.

All the compounds in the tables were found to be diamagnetic.

o-Phenanthroline nitrosyl trichlororuthenium

To a solution of 1·46 g $RuNOCl_3 3H_2O$ in alcohol was added a solution of 1·0 g *o*-phenanthroline monohydrate in alcohol. The solution immediately turned from red to brown and a finely divided brown solid separated. This mixture was heated on a waterbath for an hour. Filtration yielded a brown powder and a red solution, which on further heating with more alcohol gave more of the brown solid. The combined residues were washed with alcohol, dried in air and recrystallized from nitromethane. The compound was obtained as a brown powder. It was diamagnetic and gave a non-conducting solution in nitrobenzene (M/1000). (*Anal.* $C_{12}H_8N_2OCl_2Ru$ requires Ru, 24·2; C, 34·4; H, 1·9; N, 10·1%. Found: Ru, 24·2; C, 34·4; H, 2·0; N, 10·3%.)

α-α′-Dipyridyl nitrosyltrichlororuthenium

This compound is mentioned by MORGAN,[20] but no details of the preparation or analysis are given. It was prepared in the same way as the *o*-phenanthroline derivative above from 1·46 g $RuNOCl_3 3H_2O$ and 0·78 g dipyridyl in ethanol. The solution was heated for 30 min and filtered. The pale brown solid was diamagnetic and non-ionic in nitrobenzene (M/1000). (*Anal.* Found: Ru, 25·5%; required Ru, 25·7%.)

Nitrosylthiophenato nickel

This compound was mentioned by SCHMID[21] but no analysis or preparative details were given. Pure dry nitric oxide was passed over $Ni(C_6H_5S)_2$ (5 g) at room temperature for 4 hr. The solid changed from dark brown to green. The product was washed with 95% ethanol and dried over calcium chloride in an atmosphere of hydrogen. The compound is diamagnetic and non-ionic in nitrobenzene solution. (*Anal.* Found Ni, 29·8%; required for $NiNOC_6H_5S$: Ni, 29·7%.)

[19] G. JOHANSSON and W. N. LIPSCOMB, *J. chem. Phys.* **27**, 1417 (1957).
[20] G. T. MORGAN, *J. chem. Soc.* 569 (1935).
[21] H. SCHMID, *Angew. Chem.* **46**, 691 (1933).

J. Inorg. Nucl. Chem., 1958, Vol. 7, pp. 38 to 44. Pergamon Press Ltd., London

INFRA-RED SPECTRA OF TRANSITION METAL–NITRIC OXIDE COMPLEXES—II

COMPLEXES INVOLVING THE NO^- ION

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Abstract—Infra-red spectra and some chemical reactions have been studied of certain transition metal–nitric oxide complexes which can be formulated as containing the NO^- group. These are the cobalt nitrosopentammines, nitrosopentacyano and nitrosyl-nitrito complex ions. The structure of Fremy's salt is also discussed.

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IN the preceding paper,[1] infra-red spectra of numerous transition metal–nitric oxide complexes in which the nitric oxide can be regarded as being bound $M^- \leftarrow N^+{=}O$, have been reported.

The present paper is concerned with those complexes in which nitric oxide can be regarded as donating from the NO^- ion, i.e. $M^+ \leftarrow N{=}O^-$.

NITROSOPENTAMMINE SALTS OF COBALT

A series of compounds of the general formula $[Co(NH_3)_5(NO)]X_2$ were first prepared by SAND and GENSSLER[2] These workers discovered that the compounds existed in two isomeric forms: a black series ($X = Cl^-$, NO_3^-, and IO_3^-) which decomposed readily in water with rapid evolution of nitric oxide; and a red series ($X = Br^-$, I^-, NO_3^-, SO_4^{2-}, etc.), the members of which were far more stable, both to water and to dilute acids.

WERNER[3] considered that the red salts were dimeric with a hyponitro-type bridge:

$$\begin{bmatrix} (NH_3)_5Co \leftarrow N{=}O \\ | \\ (NH_3)_5Co \leftarrow N{=}O \end{bmatrix}^{4+}$$

whilst the black salts were simple monomeric co-ordination compounds. The evidence for these formulations was empirical, and later magnetic evidence implied that these structures could not be correct, as the magnetic moment of the black salt was reported to be between 1·44 and 2·81 B.M. A recent determination,[4] has shown that the salt was diamagnetic. This observation has been confirmed in these laboratories. The red nitrate was diamagnetic; the diamagnetism of the red nitrate, sulphate, bromide and iodide has been confirmed here also.

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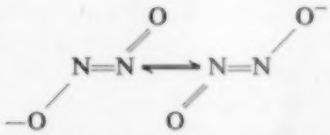
[1] J. LEWIS, R. J. IRVING and G. WILKINSON, *J. inorg. nucl. Chem.* **7**, 32 (1958).
[2] J. SAND and O. GENSSLER, *Ber. dtsch. chem. Ges.* **36**, 2083 (1903).
[3] A. WERNER and P. KARRER, *Helv. Chim. Acta* **1**, 54 (1919).
[4] R. W. ASMUSSEN, O. BOSTRUP, and J. P. JENSEN *Acta. Chem. Scand.* **12**, 24 (1958)

On the basis of the magnetic evidence, MELLOR and CRAIG[5] suggested that the black compound was dimeric with the hyponitrite structure suggested by WERNER for the red salts. In such a structure, the cobalt would be bivalent with one unpaired electron, while the nitric oxide group, which donates only two electrons to the metal atom, then pairs its remaining odd electron with another nitric oxide group to give a co-ordinated "hyponitrite." The resulting complex would then be dimeric, with one unpaired electron per cobalt atom, in agreement with the earlier magnetic evidence. However, although the black salt has been shown to be diamagnetic, the general chemical reactivity of the salt described herein is considered to agree with the formulation of the salt as a dimer. On the other hand, the red compounds were considered to be monomeric with an NO^- group co-ordinated to a Co(III) atom. Such a structure would give a diamagnetic complex, in agreement with the observed result. Earlier infra-red measurements on the black and red salts have been made by SHORT[6] who assigned a peak in the spectrum of the black chloride at 1170 cm^{-1} to the NO^- hyponitrite grouping and a peak in the red sulphate at 1080 cm^{-1} to the group. These results have now been confirmed and new evidence of the basic correctness of MELLOR and CRAIG's views has been obtained; the general behaviour of the compounds, as summarized below, is in agreement with a hyponitrite structure for the black series and a NO^- structure for the red.

Black salts

(a) In agreement with previous work[6] there is a band at 1170 cm^{-1}, both in the spectrum of the black chloride and of the black nitrate. Recent measurements[7] of the spectra of sodium, silver and mercuric hyponitrites show peaks at 1035, 1058 and 1138 cm^{-1}, respectively, which are attributed to the antisymmetric N–O stretching frequency in agreement with a *trans* configuration:



The only band in the spectra of the red salts that can be attributed to nitric oxide also falls within this region; SHORT gives a value of 1080 cm^{-1} for the red sulphate, but we have found that there is a variation from 1045 cm^{-1} in the nitrate to 1195 cm^{-1} in the iodide. Infra-red evidence therefore cannot distinguish between the NO^- and hyponitrite structures, but it does show a clear distinction from the NO^+ complexes. The absorption of the nitric oxide group in the region 1045–1195 cm^{-1} is, however, compatible with co-ordination to the metal atom of the $[N{=}O]^-$ ion, which may be expected to absorb in this region by analogy with nitrites which have a similar N—O bond order and stretching frequencies in the region of 1300 cm^{-1}.

(b) Simple hyponitrites react with carbon dioxide to form nitrous oxide, and it might have been expected that the black and red salts would behave differently towards this reagent if the above views were correct. This is so. Whilst the red salts are unaffected by CO_2 at 100°C, the black salts react to form nitrous oxide and a

[5] D. P. MELLOR and D. P. CRAIG, *J. Proc. roy. Soc. N.S.W.* **8**, (1944).
[6] L. N. SHORT, *Rev. pure appl. Chem.* **4**, 44 (1954).
[7] L. KUHN and E. R. LIPPINCOTT, *J. Amer. chem. Soc.* **78**, 1820 (1956).

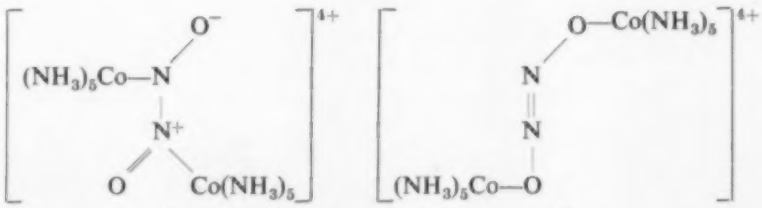
carbonato complex. Table 1 shows the effect of the carbon dioxide on the black salt: the presence of the carbonato complex is shown by the appearance of the bands at 1400 cm^{-1}, 1240 cm^{-1} and 1020 cm^{-1} in the infra-red spectrum, and the assignment of the N—O band at 1170 cm^{-1} was based on the disappearance of this band as the reaction proceeded. Nitrous oxide in the residual gas was detected both by infra-red and mass-spectrographic analysis.

TABLE 1

Assignments	(1)	(2)	(3)	(4)	(5)	(6)
NH_2/H_2O	1610(*s*, *b*)	1610(*s*, *b*)	1610(*s*, *b*)	1610(*s*, *b*)	1610(*s*, *b*)	1610(*s*, *b*)
CO_3		1400(*s*)	1405(*m*)		1400(*s*)	
NH_3	1290(*s*)	1290(*s*)	1290(*s*)	1315(*m*)	1320(*m*)	1325
			1320(*s*)			
CO_2			1240(*s*)		1245(*s*)	
NO	1170(*s*)	1170(*w*)				
CO_2		1075(*w*)	1020(*m*)		1020(*m*)	
NH_3	809(*s*)	840(*s*)	815(*m*)	840(*s*)	760(*s*)	830
					845(*s*)	

(1) $[Co(NH_3)_5(NO)]_2Cl_4$, pure.
(2) $[Co(NH_3)_5(NO)]_2Cl_4$, after five days in laboratory atmosphere.
(3) $[Co(NH_3)_5(NO)]_2Cl_4$, after two days shaking with CO_2 at 100°.
(4) $[Co(NH_3)_5(H_2O)]Cl_2$.
(5) $[Co(NH_3)_5(CO_3)]Cl$.
(6) $[Co(NH_3)_6]Cl_3$.[6]

(c) With water, the black salt becomes pink, and the infra-red spectrum shows that the product is mainly the aquopentammine with a little carbonato complex. It has always been assumed previously that the gas evolved on heating the black salt with water or dilute acid is wholly nitric oxide. Analysis of the gas after it had been treated with solid potassium hydroxide showed strong absorptions characteristic of nitrous oxide. The decomposition may then be considered to follow that of hyponitrous acid, although the production of nitric oxide is not typical of the decomposition of an alkali hyponitrite. The presence of nitric oxide may be associated with the difference in bonding of the metal and nitrogen atoms in the black salt and in the simple hyponitrites. If bonding occurs through the nitrogen atoms (I), as seems most reasonable and more in keeping with the nature of the infra-red spectrum, rather than through oxygen (II):



I II

[6] M. KOBAYASHI and J. FUJITA, *J. chem. Phys.* **23**, 1354 (1955).

then the weakening of the N—N bond in (I) may well account for the nitric oxide produced from the black salt. This does not occur with the free hyponitrous acid, which would be analogous to a structure (II).

It may be noted here that structure (I) is similar to that of Fremy's salt, which, as is well known, dissociates in water with fission of the N–N bond.*

TABLE 2

Assignments[9]	Fremy's salt $KSO_3(NO)_2$	$K_2SO_3(NO)_2$[10]
S—O	1290(*vs*)	1265–85
N—O	1262(*s*)	1230
S—O	1073(*s*) 1047(*s*)	1055
N—N—S	850(*s*)	922
S—O	658(*s*)	625

(d) Additional evidence for the hyponitrite structure is that the black chloride has been prepared (although in low yield) by addition of solid sodium hyponitrite to a solution of anhydrous cobaltous chloride in liquid ammonia.

(e) The instability of the black salts in solution may be associated with an autocatalytic decomposition by cobalt pentammine complexes. It has been observed that solutions of Fremy's salt are decolorized by certain transition metal complex ions. No effect was observed with simple cobaltous ions but immediate decolorization occurred on addition of complex cobaltic hexammines; the effect was less marked with cobalt pentammines and tetrammines.

If the dimeric structure of the black salt is correct, then the diamagnetism must arise from an interaction of the unpaired electrons on the two cobalt atoms. Such an interaction is known to occur in some binuclear complexes.

Red salts

The formulation of the red salt as having a monomolecular anion with NO^- co-ordinated to a trivalent cobalt atom is in agreement with the diamagnetism and the solubility of the salts in water. The similarity to other complex cobaltic cations of the type $[CoA_6]^{3+}$ is shown by polarography of the aqueous solutions when two well defined reduction waves are observed, the first corresponding to a one-electron reduction:

$$Co^{3+} \rightarrow Co^{2+}$$

followed by

$$Co^{2+} \rightarrow Co^{0}$$

The half-wave potentials are also similar to those observed for $[Co(NH_3)_5(NO_2)]^{2+}$[11].

* Fremy's salt exists in two forms, a paramagnetic monomer in solution and a diamagnetic solid dimer. The latter would be expected to have a structure similar to that of the black cobalt nitrosopentammine. In the infra-red spectrum of Fremy's salt (Table 2) the peak at 1262 cm^{-1} may be assigned to the N—O stretch (compared with the value of 1170 cm^{-1} for the black chloride and red nitrate) by comparison with the spectrum[9] of $K_2SO_3(NO)_2$ (Table 2).

[9] R. DRAGO, *J. Amer. chem. Soc.* **79**, 2049 (1957).

[10] T. MOELLER and G. KING, *Inorganic Syntheses* Vol. IV, p. 168. McGraw-Hill, London (1953).

[11] J. B. WILLIS, S. A. FRIEND and D. P. MELLOR, *J. Amer. chem. Soc.* **67**, 1680 (1945).

OTHER COMPLEXES CONTAINING $M^+ \leftarrow N{=}O^-$

A complex which may be considered to contain the NO^- group has been obtained by NAST[12] through interaction of the black chloride with potassium cyanide:

$$[Co(NH_3)_5(NO)]_2Cl_4 + 10KCN \rightarrow 2K_3[Co(CN_5(NO)] + 4KCl + 10NH_3$$

We have obtained this cyanide complex also by using the red sulphate or nitrate as the starting material. The cyanide is very similar to the red ammine salts—it is diamagnetic, very soluble and stable in water, and it has an absorption in the infra-red at 1120 cm^{-1}; its formulation as an NO^- derivative thus seems unequivocal.

The compound $Na_2[Co(NO_2)_4(H_2O)(NO)]$ has also been reported by NAST[13] and was considered to be a compound in which there is a solid state equilibrium between a diamagnetic (NO^-) type of complex and a paramagnetic species involving either nitric oxide or NO^+ co-ordinated to a bivalent cobaltammine residue. The latter complex would then have a magnetic moment corresponding to two unpaired electrons. The evidence for this postulate came from the low value of the observed magnetic moment, 1·3 Bohr magnetons at room temperatures, and from the marked variation of the susceptibility from the Curie–Weiss law.

We find the complex to have an intense N—O infra-red stretching frequency at 1720 cm^{-1}, which is similar to those for complexes containing the NO^+ group;[1] there is no evidence of absorption in the region 1000–1200 cm^{-1} assignable to NO^-. If the complex were considered as containing NO^+, then the cobalt would be formally in the univalent state. Thus, to allow inner orbital bonding, two electrons would have to be promoted to the 5*s* level as found in $[Ni(diarsine)_3]\ (ClO_4)_2$,[14] with the resultant formation of a diamagnetic complex

	3*d*	4*s*	4*p*	5*s*	
Co^+	⇅ ⇅ ⇅ ↑ ↑	○	○ ○ ○	○	
Co^+	⇅ ⇅ ⇅	⇅	○ ○ ○	○	in NAST's compound.

d^2sp^3 hybridization

A paramagnetic complex could result from the substitution of "outer" orbital bonding, but such bonding is not found to occur elsewhere in nitro- and nitrosyl-complexes.

An alternative and more satisfactory interpretation of the above behaviour is that NAST's original complex is $Na_2[Co(NO_2)_4(OH)(NO)]$, which is similar to the nitrosyl-hydroxy complexes of ruthenium and osmium.[1] The cobalt atom would then have only one unpaired electron and would be formally bivalent. The ready oxidation of the complex to cobaltinitrite is then understandable. The magnetic properties observed by NAST can be explained by assuming the formation of a mixture of the nitrosyl-complex and sodium cobaltinitrite. In agreement with this view, we have found that it is very difficult to prepare the nitric oxide complex in a state free from cobaltinitrite.

EXPERIMENTAL

1. *The black series*

$[Co(NH_3)_5NO]_2Cl_4$. This was made by the method of MOELLER and KING[10] and ASMUSSEN[4] from cobaltous chloride, ammonia and nitric oxide in the absence of air. (*Anal.* Required: Co, 24·08%; Found: Co, 23·80%.)

[12] R. NAST and M. ROHMER, *Z. anorg. Chem.* **285**, 271 (1956).
[13] R. NAST and M. ROHMER, *Z. anorg. Chem.* **275**, 152 (1954).
[14] R. S. NYHOLM, *J. chem. Soc.* 2602 (1951).

$[Co(NH_3)_5NO]_2(NO_3)_4$. This was made in a similar manner; 8 g of cobalt nitrate (hydrated) in 20 ml of water was treated with 50 ml of ice-cold 0·88 ammonia, the resulting solution filtered and saturated with nitric oxide for 45 min with intensive ice-cooling and in the absence of air. (If nitric oxide is passed for too long, or if the cooling is insufficient, the red salt is formed.) The black nitrate was washed with alcohol and ether, and dried *in vacuo*. (*Anal.* Required: Co, 19·76%; Found: Co, 19·3%.)

Attempts to make a black sulphate and other black salts failed, although the sulphate appears to be formed as an intermediate during preparation of the red sulphate. The black iodate should be considered as a member of the red series, as it was stable to water.

Reactions of the black salts. On standing for some time in air the black salt becomes pink and the product is mainly the aquapentammine with some carbonato complex (Table 1). The black chloride was heated with dry carbon dioxide in a closed system for about two days at 100°C. The residual gases were removed and analysed both by infra-red and mass-spectroscopy. The presence of nitrous oxide was shown by both methods—in the infra-red, bands were present at 2235(*s*), 2213(*s*), 1305(*m*) and 1275(*m*) characteristic of N_2O.[15] No NO or NO_2 was detected, even when the KOH absorption stage was omitted in the case of the infra-red measurement. Analysis by infra-red of the gas from the reaction with water showed N_2O to be present in addition to the nitric oxide found by previous workers.

2. *The red series*

$[Co(NH_3)_5NO]SO_4$. This was made in the same manner as the black chloride, from 7 g of anhydrous cobalt sulphate in 25 ml water with 40 ml ammonia. Nitric oxide was passed for 2 hr. External cooling was not necessary. (*Anal.* Required: Co, 20·48%; Found: Co, 20·43%.)

$[Co(NH_3)_5NO](NO_3)_2$. This was made in the same way as the black nitrate but without external cooling. The nitric oxide was passed for 3 hr through the solution. The salt was recrystallized twice from dilute ammonia. (*Anal.* Required: Co, 19·76%. Found: Co, 19·65%.)

$[Co(NH_3)_5NO]Br_2 \cdot 2H_2O$. This was prepared by mixing saturated solutions of the red nitrate and of potassium bromide. The resulting red precipitate was washed with ethanol and ether. (*Anal.* Required: Co, 15·90 %; Found: Co, 16·0%).

$[Co(NH_3)_5NO]Cl_2$. This was prepared by WERNER's method[3] from the bromide (silver chloride suspension with a solution of the red bromide). WERNER reported highly variable analyses—as we do—but the infra-red spectrum shows that the product contains the chloride, although rigorous purification appears to be very difficult.

$[Co(NH_3)_5NO]I_2$. This was made in the same manner as the red bromide with the nitrate and potassium iodide. The product is less soluble than the red bromide. (*Anal.* Required: Co, 12·71%; Found: Co, 12·7%.)

Reactions of the red salts. The salts are unaffected by water and some are quite soluble in it. They are also unaffected by dilute acids. There is no evidence for any reaction with carbon dioxide under the conditions with which the black salts react, nor is there any change on standing in air.

A pure sample of the red nitrate in 0·001 M solution with 0·1 N potassium sulphate as supporting electrolyte was studied using a Tilsden recording polarograph. Two reversible waves were formed with values of the potential versus the standard mercurous sulphate electrode of −0·55 and −1·41 V, respectively. Measurement of the slope of the waves allowed an estimate of the values of n from the expression

$$E_{d.e.} = E_{\frac{1}{2}} + \frac{RT}{nF}\left[\log_e \frac{i}{i_d - i}\right]$$

This gave a value of $n = 1{\cdot}2$ for the first wave and $n = 2{\cdot}0$ for the second.

The reversibility of the process was shown by the linearity of the plot of $E_{d.e.}$ against the log term.

$Na_2[Co(NO_2)_4(OH)(NO)]$. This was prepared by NAST's method[15] as deep-red crystals, but we have not succeeded in obtaining a specimen free from cobaltinitrite. The substance was found to be paramagnetic, and to be decomposed by water with evolution of nitric oxide.

$K_2[Co(CN)_5(NO)]_2H_2O$. This compound was made by NAST's method from the black pentammine nitrosyl chloride. We have found that a similar procedure using the red salts gives the identical

[15] E. L. SAIER and A. POZEFSKY, *Analyt. Chem.* **26**, 1079 (1954).

TABLE 3

	NO assigned frequencies	Other strong bands
Black series		
$[Co(NH_3)_5NO]_2Cl_4$	1170(*s*)	1610, 1290, 809
$[Co(NH_3)_5NO]_2(NO_3)_4$	1170(*s*)	1610, 1305, 1010
Red series		
$[Co(NH_3)_5NO](NO_3)_2$	1045(*m*)	1610, 1300, 930, 820
$[Co(NH_3)_5NO]SO_4$	1080*(*m*)	1610, 1300, 1120, 840
$[Co(NH_3)_5NO]I_2$	1195(*m*)	1610, 1305
$[Co(NH_3)_5NO]Br_2$	1173(*m*)	1610, 1300
$[Co(NH_3)_5NO]Cl_2$	1150(*m*)	1610, 1310
$[Co(NO_2)_4(OH)(NO)]Na_2$	1740(*vs*)	1620(*m*), 1425(*s*), 1325(*s*), 845(*m*), 835(*vs*), 830(*m*)
$[Co(NO_2)_6]Na_3$		1645(*w*), 1575(*m*), 1430(*vs*), 1333(*vs*), 847(*s*)[17]
$[Co(CN)_5(NO)]K_3$	1120(*m*)	2141(*s*), 2104(*sh*), 1630(*m*)

product. Whether the black or red salt be used, efficient ice-cooling must be maintained during the addition of the potassium cyanide to the red or black salt. An air stream must be used to remove ammonia before the complex is precipitated with methanol. (*Anal.* Required K, 31·53%; Found: K, 31·99%.)

Infra-red spectra

The spectra were measured in Nujol mulls using a Perkin–Elmer Model 21 double-beam recording spectrophotometer with sodium chloride optics. The data are given in Table 3.

Fremy's Salt: This was prepared by PALMER's[16] method.

Acknowledgements—We should like to acknowledge the help of MR. J. OXLEY who was responsible for making the polarographic measurements, and of DR. E. R. ROBERTS for the mass-spectroscopic examination. We also wish to thank the Department of Scientific and Industrial Research for a Research Studentship to one of us (W. P. G.).

* The assignment of 1080 cm^{-1} in the red sulphate to NO^-, as reported by SHORT,[6] cannot be made unequivocally since the sulphate ion absorbs heavily in this region.

[16] W. G. PALMER, *Experimental Inorganic Chemistry* p. 281. Cambridge University Press, Cambridge (1954).
[17] F. A. MILLER and C. H. WILKINS, *Analyt. Chem.* **24**, 1253 (1952).

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PREPARATION AND PROPERTIES OF $LiAu(CN)_2$, $NaAu(CN)_2$, AND THE DOUBLE COMPOUND $LiAu(CN)_2 \cdot KAu(CN)_2$*

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Abstract—Preparation and properties of $LiAu(CN)_2$, $NaAu(CN)_2$ and of the double compound $LiAu(CN)_2 \cdot KAu(CN)_2$ are presented. $LiAu(CN)_2$ is brilliant yellow and very water soluble (1·8 kg/l. at 25°C); rhombohedral cell dimensions are: $a_o = 8{\cdot}934 \pm 0{\cdot}005$ Å, $\alpha = 21°48'$. $LiAu(CN)_2 \cdot KAu(CN)_2$ is colourless, tetragonal, with $a_o = 7{\cdot}1120 \pm 0{\cdot}0006$ Å, $c_o = 8{\cdot}5896 \pm 0{\cdot}0006$ Å. An equimolar solution of $LiAu(CN)_2$ and $KAu(CN)_2$ is incongruently saturated at 25°C, depositing, on isothermal evaporation, first $KAu(CN)_2$ and later $LiAu(CN)_2 \cdot KAu(CN)_2$.

New values for the cell dimensions of $NaAu(CN)_2$ were determined. $NaAu(CN)_2$ is colourless, rhombohedral, with $a_o = 9{\cdot}24$ Å, $\alpha = 22°42'$, calculated density, 4·38, measured 4·375. The cell dimensions of an earlier publication[1] which give a calculated density of 3·39 are apparently erroneous.

No compound formation or solid solution was observed between $LiAu(CN)_2$ and $NaAu(CN)_2$.

A VERY water-soluble compound containing the $Au(CN)_2^-$ ion was needed to obtain the weaker Raman frequencies for use in frequency assignments of the $Au(CN)_2^-$ ion.[2] Preliminary work showed that $LiAu(CN)_2$ is many times more water-soluble than $KAu(CN)_2$ or $NaAu(CN)_2$. Since $LiAu(CN)_2$ has unexpected properties and has not been described previously, it seemed worth while to determine its X-ray and optical properties, and to determine whether the lithium salt is hydrated, since $Au(CN)_2^-$ salts containing the larger cations of the alkali metals are anhydrous. In addition, a systematic study of the force constants and orientation of metal-cyanide groups in the crystal lattice of many complexes is being pursued, using infra-red absorption spectra and, wherever possible, polarized infra-red absorption of single crystals.[2–7] The preparation and properties of some compounds being used in that study are reported here.

EXPERIMENTAL

Preliminary work

For the preliminary work, a small amount of $LiAu(CN)_2$ was made by passing aqueous KCN through Li^+-form cation resin (Dowex-50) and dissolving AuCN in the LiCN effluent. From the known molar extinction coefficient of the aqueous $Au(CN)_2^-$ ion in the infra-red,[8] it was easily determined even in this impure preparation (some potassium was still present) that $LiAu(CN)_2$ is many times more soluble than $KAu(CN)_2$ (a saturated solution of $KAu(CN)_2$ at 25° is 0·87 M).

* This work was sponsored by the U.S. Atomic Energy Commission.

† Deceased.

[1] E. A. SHUGAM and G. S. ZHDANOV, *Trud. Inst. Krist., Akad. Nauk SSSR* **4**, 179 (1948); *Chem. Abstr.* **47**, 6212 (1953).
[2] L. H. JONES, *J. chem. Phys.* **27**, 468 (1957)
[3] L. H. JONES, *J. chem. Phys.* **22**, 1135 (1954).
[4] L. H. JONES, *J. chem. Phys.* **25**, 379 (1956).
[5] L. H. JONES, *J. chem. Phys.* **26**, 1578 (1957).
[6] L. H. JONES, *J. chem. Phys.* **27**, 665 (1957).
[7] D. T. CROMER, *J. phys. Chem.* **61**, 1388 (1957).
[8] L. H. JONES and R. A. PENNEMAN, *J. chem. Phys.* **22**, 965 (1954).

Partial evaporation of this solution yielded colourless tetragonal crystals, with properties considerably different from those of $KAu(CN)_2$, and it was thought these crystals were $LiAu(CN)_2$. It was later found that these crystals were of the then unknown compound $LiAu(CN)_2 \cdot KAu(CN)_2$ which is much less soluble than $LiAu(CN)_2$.

Preparation of $NaAu(CN)_2$

For the preparation of $LiAu(CN)_2$ in quantity, $NaAu(CN)_2$ was chosen as the starting material since it could readily be prepared pure by recrystallization (a saturated solution of $NaAu(CN)_2$ is 0·16 M at 25°C). More than 200 g of $NaAu(CN)_2$ was prepared by dissolving equimolar amounts of AuCN and NaCN in boiling water and recrystallizing the product three times. The final product gave a neutral solution. It was a pure phase by microscopic, X-ray and analytical examination (found Au = $72{\cdot}4_4$, theory = $72{\cdot}4_2$).

Properties of $NaAu(CN)_2$

The powder X-ray diffraction pattern of the compound was indexed on the basis of a rhombohedral cell with dimensions $a_0 = 9{\cdot}24$ Å, $\alpha = 22°42'$. (The dimensions of the corresponding triply primitive hexagonal unit cell are $a_0 = 3{\cdot}64$ Å, $c_0 = 27{\cdot}0$ Å.) Assuming one formula unit per rhombohedral cell the calculated density is $4{\cdot}38_1$ g/cm³. The density measured pycnometrically using *S*-tetrabromoethane was 4·375 g/cm³.

The crystals of $NaAu(CN)_2$ are colourless, thin hexagonal plates, optically uniaxial positive with refractive indices (sodium *D* lines) $n_0 = 1{\cdot}82_3$, $n_e = 1{\cdot}83_3$ combining this information with the above cell constants gives a Lorentz–Lorenz refraction of 27·2 cm³. The value estimated from the refraction of $KAu(CN)_2$ (28·8 cm³[9]) less FAJANS value for K^+-ion (2·2 cm³), plus the value for Na^+-ion (0·50 cm³) is 27·1 cm³.

Previous workers[1] reported a hexagonal cell for $NaAu(CN)_2$ (space group D^2_{3d}) with dimensions $a_0 = 7{\cdot}2$ Å, $c_0 = 17{\cdot}8$ Å, containing six formula units, and a "calculated density based on $KAu(CN)_2$ of 3·26 g/cm³." However, we calculate a value of 3·39 g/cm³ from their cell constants. Neither of these values approaches the measured density of 4·375 g/cm³, and it is difficult to imagine polymorphs having such widely different densities. The excellent agreement between the measured and calculated densities and refractions supports the validity of the present findings, which were obtained from a carefully purified and analysed compound.

Preparation of $LiAu(CN)_2$

Li^+-form Dowex-50 resin was made by first freeing the resin from iron with HCl and neutralizing the H^+-form with Li_2CO_3. One-half mole of $NaAu(CN)_2$ as a 0·16 M solution was slowly passed through a column containing a 60 per cent molar excess of Li^+-form resin. The effluent was concentrated by evaporation until crystallization began.

Properties of $LiAu(CN)_2$

The solubility of $LiAu(CN)_2$ is 7 M at 25°C. Crystals obtained from this solution were yellow hexagonal plates and showed negligible weight loss at 110°C. Analysis for lithium and gold gave the following results (700 mg samples taken): Au 76·96

[9] E. STARITZKY and F. H. ELLINGER, *Analyt. Chem.* **28**, 420 (1956).

(theory 76·96)°, Li 2·71 (theory 2·71). This excellent agreement shows that the compound is anhydrous. It was sodium-free by spectrographic analysis. This bright yellow compound stands in contrast to salts containing the other alkali cations and the $Au(CN)_2^-$ ion, which are colourless.

The powder X-ray diffraction pattern of $LiAu(CN)_2$ bears a strong resemblance to that of $NaAu(CN)_2$. The rhombohedral cell dimensions of $LiAu(CN)_2$ are $a_0 = 8{\cdot}934 \pm 0{\cdot}005$ Å, $\alpha = 21°48'$ (the dimensions of the corresponding triply primitive hexagonal unit cell are $a_0 = 3{\cdot}38$ Å, $c_0 = 26{\cdot}16$ Å). The similarity of patterns and cell dimensions suggests that the arrangement of gold atoms is similar in $LiAu(CN)_2$ and $NaAu(CN)_2$.

In contrast to the similarity of powder patterns, the strong negative birefringence of $LiAu(CN)_2$ compared to the weak positive birefringence of $NaAu(CN)_2$ suggests that the structures are different. $LiAu(CN)_2$ is optically uniaxial negative with indices $n_0 = 2{\cdot}33$ (yellow) and $n_\epsilon = 1{\cdot}975$ (nearly colourless). To provide complete structural data on these sodium and lithium compounds, they are being studied by F. H. KRUSE of this laboratory, using single-crystal techniques.

The density of a 9·8 g sample determined pycnometrically using *S*-tetrabromoethane was 4·922 g/cm³, in good agreement with the value, 4·93 g/cm³, calculated assuming one formula unit per cell.

Preparation of $LiAu(CN)_2 \cdot KAu(CN)_2$

The work just outlined showing that $LiAu(CN)_2$ is yellow and rhombohedral indicated that the colourless tetragonal material obtained in the preliminary work (see first paragraph in the Experimental section) was either a polymorph of $LiAu(CN)_2$ or another compound perhaps, containing potassium since it had been present as an impurity in the original preparation. When pure $LiAu(CN)_2$ and $KAu(CN)_2$ were dissolved in various proportions in water and allowed to evaporate, one of the solids obtained was this colourless tetragonal phase. Properties of this phase were constant when present with either $LiAu(CN)_2$ or $KAu(CN)_2$ as the other crystalline phase. A solution containing equimolar amounts of $LiAu(CN)_2$ and $KAu(CN)_2$ deposited, on isothermal evaporation at 25°C, first $KAu(CN)_2$ and then the tetragonal compound. Solutions had to be rich in $LiAu(CN)_2$ before the tetragonal phase appeared first on removal of water.

Properties of $LiAu(CN)_2 \cdot KAu(CN)_2$

Crystals occurred as square tetragonal plates, colourless and optically uniaxial positive with indices $n_0 = 1{\cdot}73$, $n_\epsilon = 1{\cdot}80_5$. They were difficult to obtain entirely free from the last traces of the highly soluble, yellow $LiAu(CN)_2$, so that a colourless slurry of the material, when dried on a frit after removal of mother liquor, always became tinged slightly yellow as the last traces of water evaporated. The solubility of $LiAu(CN)_2$ is so high (1·8 kg/l.) that merely breathing on the crystals removes the yellow colour temporarily. After the correction for the $LiAu(CN)_2$ present, the last column in Table 1 shows excellent agreement with the formula $LiAu(CN)_2 \cdot KAu(CN)_2$.

Powder X-ray diffraction pattern of $LiAu(CN)_2 \cdot KAu(CN)_2$

The powder pattern was indexed as a primitive tetragonal cell with dimensions $a_0 = 3{\cdot}5560 \pm 0{\cdot}0003$ Å, $c_0 = 8{\cdot}5896 \pm 0{\cdot}0006$ Å, determined by least-squares using

46 $K\alpha_1$ and $K\alpha_2$ lines in the angular range $\theta = 52$–$85°$. No extraneous lines were observed which would indicate a larger cell. The density, determined pycnometrically using *S*-tetrabromoethane on a sample weighing 8·9 g, was 4·161 g/cm³. This density, together with the above cell dimensions and the formula weight of $LiAu(CN)_2 \cdot KAu(CN)_2$ (544·116), yields $0{\cdot}500_3$ as the number of formula weights per unit cell. It was obviously necessary to obtain the true cell dimensions by single-crystal methods.

TABLE 1.—ANALYSIS OF THE TETRAGONAL PHASE $LiAu(CN)_2 \cdot KAu(CN)_2$*

Analysis (wt. %)		Mole ratio to potassium	Mole ratio to (potassium—0·13 $LiAu(CN)_2$)
Li	1·36	$1{\cdot}12_7$	1·00
Au	72·69	$2{\cdot}12_2$	2·00
CN	19·15	$4{\cdot}23_3$	3·98
K	6·80†	1·00	1·00

* Crystals of the tetragonal phase were slightly encrusted with $LiAu(CN)_2$.
† Li, Au and CN were determined directly; K was obtained by difference.

Single-crystal X-ray examination of $LiAu(CN)_2 \cdot KAu(CN)_2$

A single-crystal study by R. M. DOUGLASS* of this laboratory established the cell dimensions $a_0 = 7{\cdot}1120 \pm 0{\cdot}0006$ Å (twice the value obtained from the powder work) and $c_0 = 8{\cdot}5896 \pm 0{\cdot}0006$ Å (same as that obtained from powder work). Assuming two formula units of $LiAu(CN)_2 \cdot KAu(CN)_2$ per cell, these dimensions give a calculated density of $4{\cdot}15_8$ g/cm³, compared to the measured value, 4·16 g/cm³.

Search for compound formation between $NaAu(CN)_2$ *and* $LiAu(CN)_2$

Various proportions of $NaAu(CN)_2$ and $LiAu(CN)_2$ were dissolved and evaporated until crystals formed. X-ray and optical examination of the slurry crystals showed only the two pure components in every case. Thus, it was concluded that no compound or solid solution was formed between $NaAu(CN)_2$ and $LiAu(CN)_2$. An attempt will be made to form a double compound analogous to $LiAu(CN)_2 \cdot KAu(CN)_2$ containing $LiAu(CN)_2$ as one of the constituents, but having a cation of higher atomic number than postassium so that the positions of the alkali ions in the structure can be more readily located. To this end, the Cs, Rb, and Tl(I) salts containing the $Au(CN)_2^-$ ion are being prepared.

Properties of some alkali gold dicyanides

In Table 2 are summarized the X-ray and optical properties of the lithium and sodium gold dicyanides together with those of the double compound, $LiAu(CN)_2 \cdot KAu(CN)_2$; properties of $KAu(CN)_2$ are included for completeness.[9]

Even aside from the unexpected occurrence of the double salt, $LiAu(CN)_2 \cdot KAu(CN)_2$ the detailed properties of the individual gold dicyanides containing Li, Na, K, Rb, Cs and Tl(I) are of considerable interest. For instance, the striking colour properties of $LiAu(CN)_2$ were mentioned. Preliminary work on the rest of the series has been

* Details of the single-crystal study of $LiAu(CN)_2 \cdot KAu(CN)_2$ will be the subject of a separate publication by R. M. DOUGLASS in *Acta Cryst.*

TABLE 2.—PROPERTIES OF SOME ALKALI GOLD DICYANIDES

	Density (g/cm³) Meas.	Calc.	X-ray properties $\lambda(K\alpha) = 1{\cdot}5418$ Å	Optical properties	Vol/formula unit (Å³)		Lorentz–Lorenz refraction
$LiAu(CN)_2$ form. wt. 255·98	4·922	$4{\cdot}93_1$	Rhombohedral cell, $a_0 = 8{\cdot}934 \pm 0{\cdot}005$ Å, $\alpha = 21°48'$, $Z = 1$	Bright yellow; uniaxial negative, $n_o = 2{\cdot}33$ (yellow), $n_\varepsilon = 1{\cdot}975$ (nearly colourless). Strong negative birefringence.	LiCN AuCN $LiAu(CN)_2$	53·4[10] 50·8† 86·2	(7·9) est. 19·1 29·2‡
$NaAu(CN)_2$ form. wt. 272·03	4·375	$4{\cdot}38_1$	Rhombohedral cell, $a_0 = 9{\cdot}24$ Å, $\alpha = 22°42'$, $Z = 1$	Colourless; weak positive birefringence. Similarity of patterns suggests arrangements of Au atoms in $LiAu(CN)_2$ and $NaAu(CN)_2$ are similar, but optical properties suggest that the detailed structures are dissimilar. $n_o = 1{\cdot}82_2$, $n_\varepsilon = 1{\cdot}83_3$	NaCN $NaAu(CN)_2$	51·2[11] 103·1	8·3 27·2
$KAu(CN)_2$ form. wt. 288·14	3·55	3·56	Rhombohedral cell, $a_0 = 9{\cdot}74$ Å, $\alpha = 43°52'$, $Z = 3$	Colourless; uniaxial positive, $n_o = 1{\cdot}6005$, $n_\varepsilon = 1{\cdot}6943$	KCN $KAu(CN)_2$	69·5[12] 134·3§	10·4 28·8
$LiAu(CN)_2 \cdot KAu(CN)_2$ form. wt. 544·12	4·16*	$4{\cdot}15_3$	Tetragonal cell, $a_0 = 7{\cdot}1120 \pm 0{\cdot}0006$, $c_0 = 8{\cdot}5896 \pm 0{\cdot}0006$, $Z = 2$	Colourless; uniaxial positive, $n_o = 1{\cdot}73$, $n_\varepsilon = 1{\cdot}80_5$	$LiAu(CN)_2 \cdot KAu(CN)_2$	217·2	53·6‡

* Sample contained a small amount of denser $LiAu(CN)_2$; see text.

† Volume and refractivity calculated from unpublished data obtained on crystalline AuCN by E. STARITZKY, to be published in *Anal. Chem.*

‡ As shown in the text, the Lorentz–Lorenz refraction of $NaAu(CN)_2$ has the expected value when calculated from that of $KAu(CN)_2$. However, the value for $LiAu(CN)_2$ is abnormally high, and that for $LiAu(CN)_2 \cdot KAu(CN)_2$ is low.

§ Value calculated from unpublished data obtained on crystalline KCN by E. STARITZKY, to be published in *Anal. Chem.*

[10] J. A. LELY and J. M. BIJVOET, *Rec. Trav. Chim.* **61**, 244 (1942).

[11] H. E. SWANSON and E. TATGE, *Standard X-ray Diffraction Powder Patterns*, NBS Circular 539, Vol. I, p. 79 (1953).

[12] H. E. SWANSON and E. TATGE, *Standard X-ray Diffraction Powder Patterns*, NBS Circular 539, Vol. 1, p. 78 (1953).

started, and it has been found that while the rest of the alkali salts are colourless, $TlAu(CN)_2$ also has unusual colour properties. Perhaps in the lithium and thallium compounds the colour is due to the stronger polarization of these cations. It will be interesting to learn whether the apparent gross similarities in X-ray patterns of $LiAu(CN)_2$ and $NaAu(CN)_2$ are borne out in detail when the study of their structure has been completed, especially since the qualitative inference drawn from the optical properties is that the detailed structures are dissimilar. In this connexion it should be noted that the powder X-ray diffraction pattern of $NaAu(CN)_2$ shows marked similarities to that of $KAu(CN)_2$. The hexagonal unit cell of the potassium compound appears to be related to that of the sodium compound by the transformation matrix $210/\bar{1}10/001$.

Acknowledgements—It is a pleasure to thank DR. R. M. DOUGLASS for his help with the X-ray and optical information in this manuscript which was prepared after the untimely death of E. STARITZKY. A. L. HENICKSMAN, E. H. VAN KOOTEN and R. D. GARDNER performed the analyses.

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THE THERMAL DECOMPOSITION OF YTTRIUM AND THE RARE EARTH METAL SULPHATE HYDRATES

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(*Received* 7 *November* 1957)

Abstract—The thermal decomposition of lanthanum, cerium (III), praseodymium, neodymium, samarium, gadolinium, dysprosium, holmium, erbium, ytterbium, and yttrium sulphate hydrates was studied on the thermobalance. The formation of intermediate hydrates was more pronounced with the lighter rare earth elements than with the heavier ones. The first weight loss temperatures for the hydrated salts ranged from 40 to 110°C, while the minimum temperatures for the anhydrous metal sulphate levels ranged from 155 to 295°C.

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THE rare earth metal sulphates crystallize from aqueous solution at room temperature mainly as the 8-hydrates. On heating the 8-hydrates in air, they evolve the water of hydration readily. The thermal decomposition pattern goes through the following stages: metal sulphate hydrate $\xrightarrow{I}$ anhydrous metal sulphate $\xrightarrow{II}$ basic metal sulphate $\xrightarrow{III}$ metal oxide. Some question exists as to the temperature limits for the various stages of decomposition. The temperature limits for stage I have been set between 250 to 650°C;[1] stage II about 900°C;[2] and stage III at about 1600°C. The values for the last two stages are known with far less certainty than for the first stage.

Since the rare earth metal nitrate and chloride hydrates[3,4] have previously been studied on the thermobalance, it was of interest to extend these studies to include the metal sulphate hydrates as well. Because the maximum temperature limit of the thermobalance was ~900°C, this study was confined only to the determination of the temperature limits for the dehydration process. When a higher temperature furnace becomes available, it is planned to study the thermal decomposition of the anhydrous metal sulphates as well.

EXPERIMENTAL

Thermobalance

An automatic recording thermobalance with a linear heating rate of 5·4°C per minute was used.[5] Sample sizes ranged from 85 to 100 mg and were run in duplicate or triplicate. During the pyrolysis, a slow stream of air was passed through the furnace.

Chemicals

All of the rare earth compounds, except cerium, were obtained as the oxides of 99·9 per cent purity from the Lindsay Chemical Co., West Chicago, Ill.; Research

[1] J. W. MELLOR, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry* Vol. V, Chap. XXXVIII. Longmans, Green & Co., London (1924).
[2] L. WOHLER and M. GRUNZWEIG, *Ber. dtsch. chem. Ges.* **46**, 1726 (1913).
[3] W. W. WENDLANDT, *Anal. Chim. Acta* **15**, 435 (1956).
[4] W. W. WENDLANDT, *J. inorg. nucl. Chem.* **5**, 118 (1957).
[5] W. W. WENDLANDT, *Analyt. Chem.* **30**, 56 (1958).

Chemicals, Inc., Burbank, Calif.; and Research Laboratories, Inc., Newtown, Ohio. The cerium salt was obtained as $CeCl_3 \cdot 6H_2O$ from the above sources. The purity of the compounds was that listed by the supplier.

Preparation of the rare earth sulphate hydrates

The metal sulphate hydrates, except cerium, were prepared by dissolving about 0·3 g of the metal oxides in 20 ml of hot 3M sulphuric acid. After dissolution, the resulting solutions were filtered and placed in a vacuum desiccator over concentrated

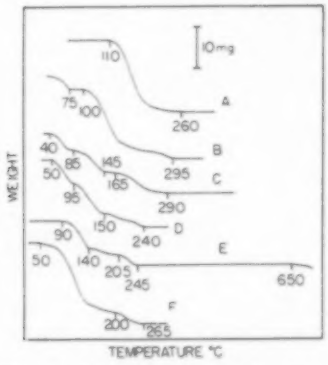

FIG. 1.—Thermal decomposition curves of the metal sulphate hydrates.
A. $Gd_2(SO_4)_3 \cdot 8H_2O$
B. $Sm_2(SO_4)_3 \cdot 8H_2O$
C. $Nd_2(SO_4)_3 \cdot 8H_2O$
D. $Pr_2(SO_4)_3 \cdot 8H_2O$
E. $Ce_2(SO_4)_3 \cdot 5H_2O$
F. $La_2(SO_4)_3 \cdot 9H_2O$

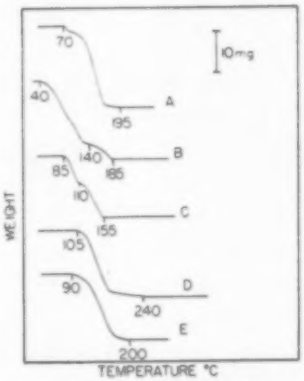

FIG. 2.—Thermal decomposition curves of the metal sulphate hydrates.
A. $Y_2(SO_4)_3 \cdot 8H_2O$
B. $Yb_2(SO_4)_3 \cdot 11H_2O$
C. $Er_2(SO_4)_3 \cdot 8H_2O$
D. $Ho_2(SO_4)_3 \cdot 8H_2O$
E. $Dy_2(SO_4)_3 \cdot 8H_2O$

sulphuric acid and allowed to crystallize. The crystals were filtered off into sintered porcelain crucibles, washed twice with 10 ml of water and once with 10 ml of 95 per cent ethyl alcohol. After air drying for 4 hr the crystals were ground to a fine powder and decomposed on the thermobalance.

Cerium sulphate was prepared in a similar manner except that the chloride was first treated with 5 ml of 10 M sulphuric acid, heated to expel the hydrogen chloride gas, 20 ml of water was added, and the resulting solution allowed to crystallize in a desiccator.

DISCUSSION

The thermal decomposition curves of the yttrium and rare earth sulphate hydrates are given in Figs. 1 and 2 with the composition data given in Table 1.

Even with the fairly rapid heating rate employed, intermediate hydrates containing 5 and 2 moles of water per mole of metal sulphate were observed. This tendency towards intermediate hydrate formation was more pronounced with the lighter rare earths; i.e. those from lanthanum to samarium. While those above samarium, with only two exceptions, decomposed directly to the anhydrous metal sulphates.

In only one case was decomposition of the anhydrous metal sulphate noted. This was with cerium (III) sulphate where sulphur trioxide began to come off at 650°C to form the basic sulphate. From the study of the thermal decomposition of cerium

(III) nitrate 6-hydrate,[3] such behaviour was expected to occur at a lower temperature with cerium (III) sulphate than with the other rare earth metal sulphates.

TABLE 1.—THE THERMAL DECOMPOSITION OF THE RARE EARTH SULPHATES; COMPOSITION DATA

Rare earth metal	$M_2(SO_4)_3 \cdot 8H_2O$		Composition, % $M_2(SO_4)_3$ $M_2(SO_4)_3 \cdot 5H_2O$		$M_2(SO_4)_3 \cdot 2H_2O$	
	Theor.	Found	Theor.	Found	Theor.	Found
Lanthanum	77·72($9H_2O$)	77·7 77·6			94·01	95·3 95·5
Cerium (III)			86·32	86·5 86·7	94·04	94·4 95·0
Praseodymium	79·81	79·3 79·3	86·35	85·6 85·4		
Neodymium	80·00	80·8 80·6	86·49	86·3 86·9	94·12	93·5 94·0
Samarium	80·34	81·1 80·5				
Gadolinium	80·68	81·1 81·4				
Dysprosium	80·96	80·9 81·6				
Holmium	81·09	81·5 81·4				
Erbium	81·20	81·3 81·0	87·36	88·5 87·8		
Ytterbium	76·19($11H_2O$)	76·3 74·5			92·82	93·5 93·6
Yttrium	76·38	77·0 77·2				

Lanthanum sulphate (Fig. 1/*F*).

According to the composition data in Table 1, lanthanum sulphate crystallized from solution as $La_2(SO_4)_3 \cdot 9H_2O$ and not as the 8-hydrate. Such a hydrate is known.[6] The first weight loss began at 50°C with a break in the curve at 200°C which corresponded approximately to the 2-hydrate. The salt was completely dehydrated at 265°C, much lower than the previously reported 600°C.[1]

[6] R. C. VICKERY, *Chemistry of the Lanthanons* p. 235. Academic Press, New York (1953).

Cerium (III) *sulphate* (Fig. 1/*E*).

The 5-hydrate, instead of the 8-hydrate, was crystallized out of solution. The first weight loss of the 5-hydrate was observed at 90°C with an intermediate break in the curve at 140°C which corresponded approximately to the 2-hydrate. The anhydrous metal sulphate weight level began at 245°C. At 650°C the metal sulphate began to lose SO_3 to form a basic salt. However, the pyrolysis was not completed far enough to obtain the basic metal sulphate weight level.

Praseodymium sulphate (Fig. 1/*D*).

The 8-hydrate began to lose weight at 50°C to give a break in the curve at 95°C which corresponded approximately to the 5-hydrate. Another break in the curve was observed at 150°C but the composition did not correspond to the stoicheiometry for the 2-hydrate. The anhydrous metal sulphate level began at 240°C.

Neodymium sulphate (Fig. 1/*C*).

The 8-hydrate began to lose weight at 40°C. Two intermediate breaks in the curve were observed, one at 85°C and the other at 145°C, corresponding to the 5- and 2-hydrates, respectively. The anhydrous metal sulphate level began at 290°C.

Samarium sulphate (Fig. 1/*B*).

The 8-hydrate, after losing loosely held water, began to decompose at 100°C. The anhydrous metal sulphate level was obtained at 295°C. Unlike the other lighter rare earths, breaks in the curve were not observed which would indicate intermediate hydrates.

Ytterbium sulphates (Fig. 2/*B*).

The composition data for ytterbium sulphate corresponded to that of $Yb_2(SO_4)_3 \cdot 11H_2O$, rather than the 8-hydrate. The thermal decomposition curve shows that the crystallized salt is probably a definite hydrate. If the salt were the 8-hydrate containing occluded water, a curve similar to that of samarium sulphate (Fig. 1/*B*) would have been obtained. The 11-hydrate began to lose water at 40°C, somewhat lower than the initial dehydration temperatures for the other heavier rare earth sulphate hydrates. A break appeared at 140°C which corresponded approximately to the 2-hydrate. The anhydrous metal sulphate level began at 185°C.

Other metal sulphates

The gadolinium (Fig. 1/*C*), dysprosium (Fig. 2/*E*), holmium (Fig. 2/*D*), and yttrium sulphate 8-hydrates (Fig. 2/*A*) decomposed directly to yield the anhydrous metal sulphates without any evidence for the formation of intermediate hydrates. The thermal decomposition curve for erbium sulphate 8-hydrate (Fig. 2/*C*) had a break at 110°C which corresponded to the 5-hydrate. Decomposition of this hydrate resulted in the formation of the anhydrous metal sulphate.

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THE INTERACTION OF URANIUM TETRACHLORIDE WITH HYDRAZINE, AMMONIA AND AMINES*

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(*Received* 5 *July* 1957)

Abstract—Equilibrium vapour-pressure studies at 35° to 55° of the systems UCl_4–$m\,RNH_2$ (R = H, CH_3, C_2H_5, n-C_3H_7) in the range of $m = 2$ to 5 revealed a univariant behaviour indicating a solid solution of UCl_4 in the corresponding ligand. At $m = 4$ the ligand pressure increases very rapidly with further increase in the ligand composition indicating the approach of a saturation limit. Evidence obtained from X-ray and thermal desorption studies indicates the existence of addition compounds of the stoicheiometry: $UCl_4 \cdot 2NH_3$, $UCl_4 \cdot 2CH_3NH_2$, $UCl_4 \cdot C_2H_5NH_2$, $UCl_4 \cdot 2C_2H_5NH_2$, and $UCl_4 \cdot n$-$C_3H_7NH_2$. The addition compounds $UCl_4 \cdot 6N_2H_4$ and $UO_2 \cdot N_2H_4$ also seem to exist although the latter was not isolated. All of the above-mentioned systems appear to be stable indefinitely when stored in sealed ampoules. They react, however, with water vapour and oxygen to give either UO_2 or UO_2Cl_2 and ligand hydrochloride as the solid products. The enthalpy, free energy and entropy of formation in UCl_4–amine systems were found to increase with increasing alkyl chain length. The values of these thermodynamic quantities at a given composition, however, depend on the history of preparation of the initial solid phase. A considerable improvement of the UCl_4 X-ray powder diagram was observed after some gaseous amine was added to the solid UCl_4 at room temperature to form a second, solid UCl_4–RNH_2 phase. The infra-red spectrum of $UCl_4 \cdot 4n$-$C_3H_7NH_2$ differs from the spectra of its components by having some additional absorption peaks. Since not enough is known at present concerning characteristic U–N absorption frequencies no specific assignment of peaks was made.

MANY co-ordination compounds of uranium salts have been prepared in which oxygen is the atom through which a ligand is co-ordinated to uranium. Little information was found in the published literature on co-ordination compounds of uranium in which the co-ordinating atom is nitrogen. Consequently, the present work was undertaken to investigate some binary systems of solid uranium tetrachloride with some simple anhydrous ligands containing nitrogen as the electron-donating atom. The ligands employed were methylamine, ethylamine, *n*-propylamine, hydrazine and ammonia. The systems UCl_4–NH_3 and UO_2Cl_2–NH_3 have been previously reported in the literature.[1]

Investigation proceeded along the following lines: (a) preparative procedures for the system (b) possible reactions between the components of the system (c) some of the chemical and physical properties of the systems at ordinary temperatures

* In part taken from a Ph.D thesis submitted by ILMARS KALNINS to the Graduate School of Illinois Institute of Technology, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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[1] P. SPACU, *Z. anorg. Chem.* **230**, 181 (1936).

(d) correlation of the stabilities of the systems with the length of the alkyl chain in the co-ordinating amine.

EXPERIMENTAL

Materials. The starting material for the preparation of anhydrous UCl_4 was pure UO_3 obtained by thermal decomposition of uranium peroxide, $UO_4 \cdot 2H_2O$.[2] Pure anhydrous UCl_4 was prepared by refluxing UO_3 with hexachloropropene[3] and subliming the UCl_4 from the solid mixture of the reaction products at 10^{-4} mm and 500°. Calc. for UCl_4: U, 62·67; Cl, 37·33. Found: U, 62·63; Cl, 37·10. The water content was negligible (0·2 per cent) in fresh preparations but rose to approximately one per cent in samples that had been stored for a year or more.

Anhydrous ammonia, methylamine and ethylamine were obtained as anhydrous compressed gases of minimum 96 per cent purity. Before use these were dehydrated by passing them through a drying tower filled with granular CaH_2. The purity of the gases was checked on a vacuum line by measuring their equilibrium vapour-pressures at 0·0° or −78·5° and comparing the values obtained with literature values.[4]

Where necessary, the gases were purified by fractional condensation. The liquid amines were first refluxed with solid CaH_2 for one to two hours and then distilled directly into container bottles. Only the middle fraction consisting of about one-half of the total distillate was taken as the pure sample.

Commercial anhydrous hydrazine (100 g) was refluxed with 150 g of lump BaO in a nitrogen atmosphere for 2 to 4 hr at 100° to 110°.[5] It was then distilled under reduced pressure (10 mm) in a closed system into a trap cooled by Dry Ice. To obtain nearly anhydrous (99·7 to 100·0 per cent) hydrazine the above procedure usually had to be repeated. The hydrazine used in most experiments was better than 99·5 per cent pure.

Apparatus and procedure. The preparative methods consisted of bringing the respective components together under exclusion of air and moisture. In all cases a 5 to 20 molar initial excess of ligand was used. The components were caused to react at room temperature either in a vacuum line or a flow system using dry N_2 as a carrier gas, or at elevated temperatures and pressures (below 200° and 50 atm) in a stainless steel bomb. After removal of the excess amine the residual product was analysed and used for further experiments.

The apparatus employed for equilibrium vapour-pressure determinations consisted of a stainless steel mortar and pestle incorporated in the sample holder of the equilibration cell. The sample holder was a 1 in. diameter industrial Pyrex glass pipe cap held against an annular stainless steel flange by means of 8 machine screws (10/24 × 1 in.) with a Teflon gasket in between. A stainless steel bellows soldered to the top of the flange served as an actuator for the metal pestle. This pestle, also of stainless steel, was soldered through the top of the bellows. A Kovar seal through the side of the flange connected the above portions of the apparatus to

[2] J. J. KATZ and E. RABINOWITCH, *The Chemistry of Uranium, National Nuclear Energy Series* Div. VIII, Vol. 5, pp. 291–292 and 314. McGraw-Hill, New York (1951).
[3] J. J. KATZ and E. RABINOWITCH, *Ibid.* p. 486.
[4] R. T. SANDERSON, *Vacuum Manipulation of Volatile Compounds* pp. 123–149. Wiley, New York (1948).
[5] C. F. HALE and F. F. SHETTERLEY, *J. Amer. chem. Soc.*, **33**, 1071 (1911).

a differential manometer in which the mercury level could be lowered, as necessary, to admit or withdraw the volatile ligand. An oil thermostat of 10 l. capacity, mounted on a large vice screw, could be raised to immerse the entire equilibration cell and manometer. In this way the whole UCl_4–amine system could be maintained at the same temperature. The temperature of the thermostat was controlled to $\pm 0{\cdot}05°$ with two heaters (150 and 200 W), a water cooled copper coil and an E. H. Sargent and Co. Thermonitor, Model S. Temperatures were read on a calibrated thermometer with an accuracy of $\pm 0{\cdot}02°$. Mercury levels were measured within $\pm 0{\cdot}05$ mm by means of a cathetometer. The reliability of the apparatus was checked by reproducing the well known phase diagram of the $CuSO_4$–H_2O system at 50·0°. Pressure readings obtained agreed with published values within 2 mm.

The equilibrium pressures were obtained at three or four different temperatures in the range of 35° to 75°. Each pressure reading represented an apparently true equilibrium condition inasmuch as the point determined was approached from a temperature above as well as below the equilibration temperature. By rotating the pestle the equilibration rate was considerably increased compared to the equilibration rate of the unground material. An equilibrium point seemed to be established in about 10–12 hr.

A faster equilibration occurred when a system of approximate composition $UCl_4 \cdot 2(\pm 0{\cdot}2)RNH_2$ was used, which was obtained by treating UCl_4 with excess amine at elevated temperature and pressure in a pressure bomb and, subsequently, thermally decomposing the saturated solid system to the composition desired. Thus the equilibration times were reduced by a factor of 4 to 6. These rapidly equilibrating UCl_4–RNH_2 systems are denoted as "pretreated" in order to differentiate them from other systems of similar composition, employing pure UCl_4 as the initial starting phase, which are termed "non-pretreated".

To observe changes in the lattice structures of the materials dealt with in the present work, X-ray powder diagrams were taken. Attempts to obtain single crystals by recrystallization from organic solvents or from excess ligand for a more complete study of some systems were unsuccessful.

For infra-red studies a Perkin–Elmer 21, double beam spectrophotometer having NaCl optics was employed.

Analyses. For the most part standard volumetric and gravimetric procedures were employed. Total uranium content was determined by ignition of the sample to U_3O_8 at 800 to 900°,[6] uranium (IV) by titration with standard potassium dichromate[7] and chlorine by the Volhard method;[8] using either Fe(III) solution as an internal indicator or, alternately, potentiometric indication by means of a Serfass Electron Ray Titration Unit (A. H. Thomas Co.). U(IV) which interferes with the chloride titration was oxidized with an excess of 10 per cent, aqueous ferric alum solution. Free ammonia and amines or their ions were determined by acid titration with standard $HClO_4$ in dioxane, employing anhydrous acetic acid as the reaction medium.[9] Uranium ion does not interfere. Hydrazine was determined

[6] C. J. Rodden, *Analytical Chemistry of the Manhattan Project, National Nuclear Energy Series* Div. VIII, Vol. 1, p. 46. McGraw-Hill, New York (1950).
[7] I. M. Kolthoff and J. J. Lingane, *J. Amer. chem. Soc.* **55**, 1871 (1933).
[8] H. Biltz and W. Biltz, *Ausfuehrung Quantitativer Analysen* (5th Ed.) p. 145. Verlag S. Herzel, Zuerich (1947).
[9] S. Fritz, *Analyt. Chem.* **24**, 300 (1952).

by direct titration with potassium iodate in presence of Wool Red Dye as an internal indicator.[10] Small quantities of water were determined by titration with Karl Fisher reagent.[11]

RESULTS AND DISCUSSION

It was found that UCl_4 and gaseous ligand reacted reversibly to form solid $UCl_4 \cdot m$ ligand. No side reactions (e.g. solvolysis) were observed up to 200°.

UCl_4–N_2H_4 *System.* In this system products of the composition $UCl_4 \cdot 6N_2H_4$ or $UCl_4 \cdot 7N_2H_4$ were obtained. The latter compound upon standing in vacuum loses one mole of N_2H_4 to yield $UCl_4 \cdot 6N_2H_4$. Both compounds are light grey in colour. In a sealed glass ampoule the $UCl_4 \cdot 6N_2H_4$ did not change in colour for a period of over 3 years. Some representative analyses follow:

$UCl_4 \cdot 7N_2H_4$	U,	calc. 39·4; found 38·6
	Cl,	calc. 23·5; found 23·3
	N_2H_4,	calc. 37·1; found 37·0
$UCl_4 \cdot 6N_2H_4$	U,	calc. 41·6; found 41·7
	Cl,	calc. 24·8; found 24·4
	N_2H_4,	calc. 33·6; found 33·0

Since this system was extremely reactive with gaseous water and oxygen at room temperature no equilibrium vapour-pressure studies were attempted.

Phase equilibria in UCl_4–RNH_2 *systems.* To determine the effect of the alkyl chain length on the stability of UCl_4–RNH_2 systems, where R = H, CH_3, C_2H_5, n-$C_3H_7NH_2$, isothermal vapour-pressure measurements at 35°, 45° and 55° were made. The data are represented by Figs. 1, 2, 3, and 4.

The pressure-composition diagrams indicate the existence of solid solutions of the systems in the temperature and pressure range of investigation. The ligand vapour-pressure of the systems increases rapidly as the mole ratio approaches the value of four indicating saturation of the solid system. A further increase in the ligand pressure would probably lead to liquefaction of the ligand. No amine addition compounds seem to exist in this range. NH_3 may possibly form an addition compound of mole ratio of six at room temperature between 500 and 760 mm. This pressure range, however, was not investigated. The results of SPACU[1] reporting the compounds $UCl_4 \cdot 3NH_3$ and $UCl_4 \cdot 4NH_3$ could not be confirmed, although there may be a phase rearrangement at the composition $UCl_4 \cdot 3NH_3$ as judged by the corresponding phase diagram at 55°. A similar behaviour is observed in the mole ratio region of two and three in the UCl_4–n-$C_3H_7NH_2$ system.

It was found that at mole ratios in the neighbourhood of four and above the vapour-pressures coincided for both pretreated and non-pretreated samples. At lower mole ratios in the non-pretreated system the equilibrium pressures, determined after each successive addition of ligand to the solid phase, were higher than those obtained upon successive removal of the ligand from the solid phase after its equilibration with an excess of gaseous ligand. The latter, however, were essentially the same as the pressures obtained for the corresponding pretreated system. The observed pressure difference between non-pretreated and pretreated system appeared

[10] G. F. SMITH and C. S. WILCOX, *Industr. engng. Chem.* (*Anal.*) **14**, 49 (1942).
[11] J. MITCHELL, JR. and D. M. SMITH, *Aquametry*. Interscience, New York (1948).

to be due to a different state of the solid phase and not to a non-equilibrium condition. When the temperature of equilibration was returned to the previous value after having been altered, the system re-equilibrated to give the previous pressure reading within 0·15 mm. This reading did not decrease to any measurable extent for a period of several days.

In the course of the study, pressure-composition data were also collected at

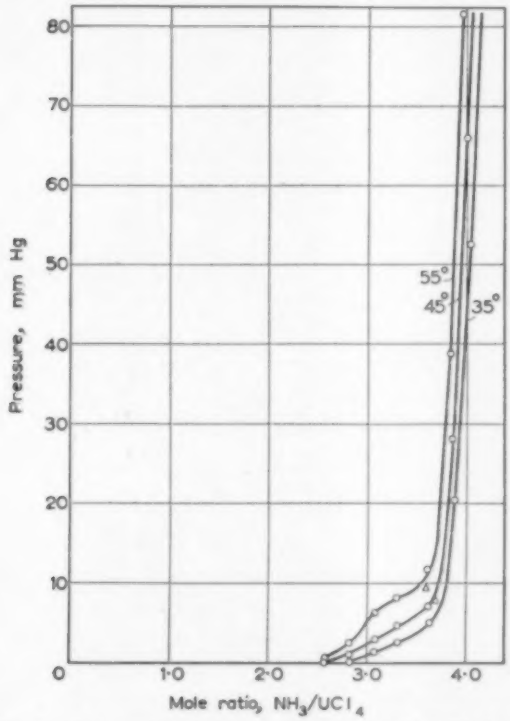

FIG. 1.—Pretreated. Initial mole ratio (m.r.) of the solid phase = 2·07.

temperatures other than those mentioned above. These were used in the calculation of the partial molar enthalpies $\Delta\bar{H}_2$, of the ligands and are not reported here. Since all of the systems exhibited a univariant behaviour within the measured pressure-composition range, the partial molar enthalpies, $\Delta\bar{H}_2$, free energies, $\Delta\bar{F}_2$, and their differences, $T\Delta\bar{S}_2$, for the ligand were calculated by the following standard thermodynamic relationships:

$$\Delta\bar{H}_2 = 2{\cdot}303\ R\,\frac{d(\log p)}{d(1/T)},$$

$$\Delta\bar{F}_2 = 2{\cdot}303\ RT\log P,$$

$$T\Delta\bar{S}_2 = \Delta\bar{H}_2 - \Delta\bar{F}_2;$$

where, the gas constant $R = 1{\cdot}987$ cal/mole°, $T = 308{\cdot}2°$ K(35°), P = pressure in atm, p = pressure in mm. The $\frac{d(\log p)}{d(1/T)}$ values were calculated from the linear plots

of log p *vs.* $1/T$ obtained from the p and T data. Pure, solid UCl_4 at 308·2° K and pure ligand in the ideal gas state at 308·2° K and 1 atm were the standard reference states of the components. The probable error in $\Delta\bar{H}_2$ was estimated at $\pm$0·2 kcal/mole and the probable error in $\Delta\bar{F}_2$ as $\pm$0·01 kcal/mole. The probable error in the $T\Delta\bar{S}_2$ value then also was $\pm$0·2 kcal/mole. The partial molar quantities thus obtained may be summarized as follows.

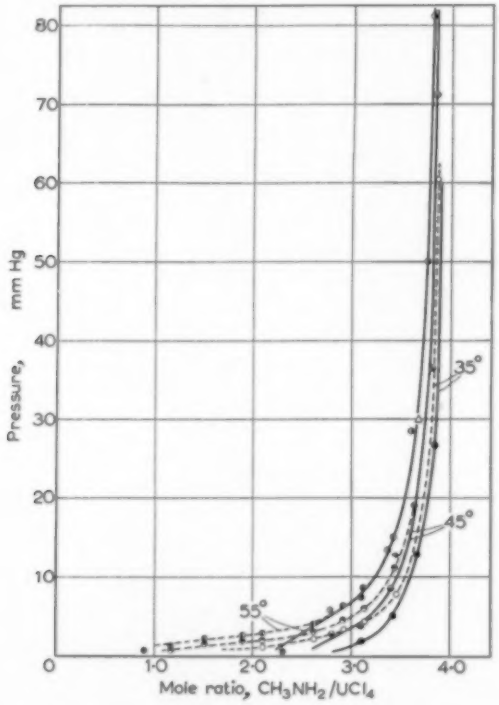

FIG. 2.—Pretreated. Initial mole ratio of the solid phase = 1·75.
○ Experimental points of the pretreated system at 35·00°
◓ Experimental points of the pretreated system at 45·00°
◐ Experimental points of the pretreated system at 55·00°
● Experimental points of the non-pretreated system at 35·00°
◒ Experimental points of the non-pretreated system at 45·00°
◑ Experimental points of the non-pretreated system at 55·00°
△ Experimental points obtained after addition of excess ligand and subsequent removal of the excess. (The analogous points in Figs. 1 and 3 have the same meaning.)

In non-pretreated systems, $\Delta\bar{H}_2$, was found to be nearly constant over the range of $m = 0{\cdot}8$ to $m = 3{\cdot}6$. An evaluation of $\Delta\bar{H}_2$ by the method of least squares gave the following equations,

$$UCl_4\text{–}CH_3NH_2, \quad \Delta\bar{H}_2 = -7{\cdot}72 + 0{\cdot}24m.$$

$$UCl_4\text{–}n\text{-}C_3H_7NH_2 \quad \Delta\bar{H}_2 = -1{\cdot}12 - 0{\cdot}055m.$$

Extending the applicable composition range to $m = 4$, the standard enthalpies of

reaction were obtained by integration of the above equations according to the thermodynamic relationship, that $\Delta H = \int_{m1}^{m2} \Delta \bar{H}_2 dm$. For the reactions:

$$UCl_4 + 4CH_3NH_2 \rightarrow UCl_4 \cdot 4CH_3NH_2; \qquad \Delta H = -29{\cdot}1 \pm 0{\cdot}5 \text{ kcal/mole}$$

$$UCl_4 + 4C_3H_7NH_2 \rightarrow UCl_4 \cdot 4n\text{-}C_3H_7NH_2; \quad \Delta H = -4{\cdot}9 \pm 0{\cdot}5 \text{ kcal/mole}$$

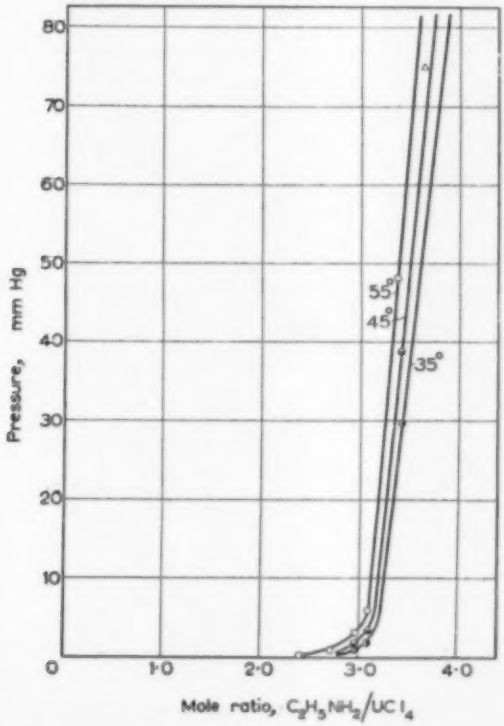

FIG. 3.—Pretreated. Initial mole ratio of the solid phase = 1·80 ± 0·03.

The $\Delta \bar{F}_2$ values for the above non-pretreated systems increased but slowly in the range of $m = 1$ to $m = 4$. The free energies of reaction at 35·0° per mole of solid UCl_4, ΔF, were calculated by means of the two thermodynamic relationships, $\Delta F = \int_{m1}^{m2} \Delta \bar{F}_2 dm$, in the range of $m_1 = 0{\cdot}9$ to $m_2 = 4{\cdot}0$ for CH_3NH_2 and of $m_1 = 0{\cdot}7$ to $m_2 = 4{\cdot}0$ for n-$C_3H_7NH_2$ and $\Delta F = \Delta \bar{F}_1 + m\Delta \bar{F}_2$, below $m_1 = 0{\cdot}9$ or 0·7, respectively. It was found that $\Delta F = -16{\cdot}8 \pm 0{\cdot}5$ kcal/mole for the methylamine case and $\Delta F = -9{\cdot}5 \pm 0{\cdot}5$ kcal/mole for n-propylamine case. The standard entropy of reaction, ΔS, at 35·0° was found equal to $-39{\cdot}9 \pm 3{\cdot}2$ cal/mole°C for the former and $+14{\cdot}9 \pm 3{\cdot}2$ cal/mole°C for the latter reaction. The ΔF values indicate that the $UCl_4 \cdot 4n\text{-}C_3H_7NH_2$ in which the alkyl chain is longer is considerably less stable than the $UCl_4 \cdot 4CH_3NH_2$ of shorter chain length, provided the initial solid phase is pure UCl_4. The longer alkyl chain is also responsible for the positive entropy of reaction which contributes substantially to the stability of the UCl_4–n-$C_3H_7NH_2$

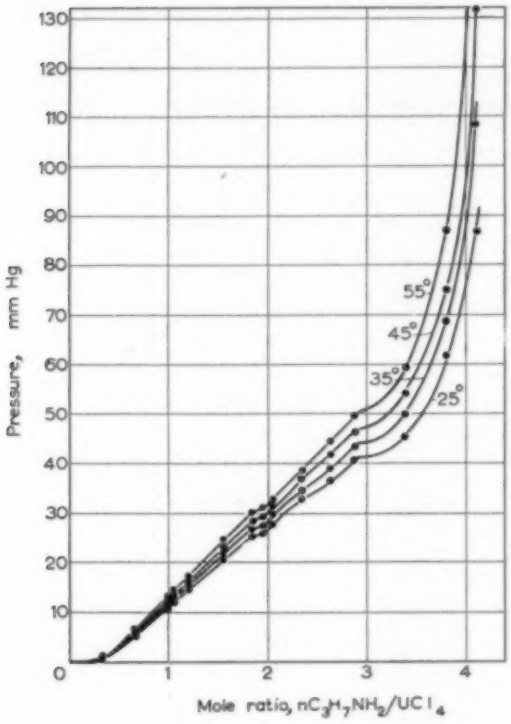

FIG. 4.—Non-pretreated.

system. The heat of reaction decreases considerably with increase in the alkyl chain-length, presumably due to steric forces among the alkyl groups and other atoms of the lattice.

For pretreated systems in which the initial solid phase was a thermally decomposed UCl_4–RNH_2, none of the thermodynamic quantities remained constant with change in composition. The $\Delta\bar{H}_2$ values which increased rapidly as the mole ratio increased from $m = 2$ to 4 were initially large and negative. At $m = 4$, $\Delta\bar{H}_2$ became constant over a short range continuing to increase thereafter but to a lesser extent than before. No extrapolation to $m = 0$ could be reasonably performed. The increase in $\Delta\bar{H}_2$ was approximately linear between $m = 2$ and $m = 3{\cdot}7$. At $m = 2{\cdot}8$, for example, $\Delta\bar{H}_2$ was approximately the same, $-15{\cdot}5$ kcal/mole for the three ligands, NH_3, CH_3NH_2 and $C_2H_5NH_2$. The difference in $\Delta\bar{H}_2$ between pretreated and non-pretreated UCl_4–CH_3NH_2 at this point was about $-7{\cdot}5$ kcal/mole. For the reaction, $UCl_4{\cdot}2CH_3NH_2 + 2CH_3NH_2 \rightarrow UCl_4{\cdot}4CH_3NH_2$; $\Delta H = -27 \pm 1$ kcal/mole. For the same reaction in the non-pretreated system $\Delta H = -14{\cdot}0 \pm 0{\cdot}5$ kcal/mole. The change in lattice energy due to lattice disorder thus is approximately -13 kcal/mole. It is a common observation that solids prepared by thermal decomposition of other solids at relatively low decomposition temperatures exhibit a greater reactivity than when prepared by other methods. Such solids are often said to be in their "active" forms. It seems that such increased reactivity is at least partially due to increase in the strain-energy of such a solid.

The behaviour of $\Delta\bar{F}_2$ and $T\Delta\bar{S}_2$ with respect to composition was approximately similar to that of $\Delta\bar{H}_2$ described above. The corresponding integral quantities, ΔF and ΔS could not be calculated. At $m > 4$ the $\Delta\bar{H}_2$ and $\Delta\bar{F}_2$ became respectively identical in both the pretreated and the non-pretreated system.

At compositions below $m = 2$ the pressures were too low to be measured by means of a mercury manometer. Systems at such compositions were, therefore, investigated by means of X-ray powder diagrams. All of the samples used in the X-ray studies were analysed for their amine content and their mole ratio composition calculated. The X-ray diagram of any of the above systems was considerably more complex than that of UCl_4. Apparently these systems have a lower crystal symmetry than UCl_4 (tetragonal).[12] In addition, the diffraction lines were rather broad and the background was quite heavy so that attempts to index these diagrams were soon abandoned. The lines of each system were inter-compared with respect to the line position, distribution and intensity. Above $m = 3$ the lines usually were diffuse and very weak in intensity. As a result of these X-ray investigations the addition compounds represented by the formulae $UCl_4 \cdot 2CH_3NH_2$, $UCl_4 \cdot C_2H_5NH_2$, $UCl_4 \cdot 2C_2H_5NH_2$, $UCl_4 \cdot n\text{-}C_3H_7NH_2$ were assigned to the phases observed. The longer the alkyl chain in the amine the more the solid phase behaves like a solid solution. Apparently, even at low mole ratios, the long carbon chain provides so much steric hindrance that there is no longer a well-defined co-ordination sphere around the U(IV) ion and no phase characteristic of a stoicheiometric compound. Furthermore, the longer the alkyl chain the lower was the composition at which the X-ray pattern became liquid-like in appearance. The so-called liquid-like pattern is characterized by a few broad, diffuse regions on a heavy film background. These regions have replaced the strongest lines observed in the appropriate lower mole ratio systems. For methylamine and ethylamine this phenomenon was observed above $m = 3$ but for the propylamines it began above $m = 2$.

The addition of a small quantity of any of the amines ($m \simeq 0{\cdot}5$) to solid UCl_4, which had a satisfactory but by no means a good line diagram, gave an extremely sharp UCl_4 line pattern up to a Bragg angle of 90°. Some broad and weak lines of another phase also were observed but they were too different in appearance to be confused with the UCl_4 lines. X-ray diagrams of stationary samples disclosed that relatively large crystallites, estimated as between 10^{-3} and 10^{-2} cm in grain size, formed the sharp UCl_4 pattern. The most probable explanation is that the ligand has preferentially attacked the smaller and the more disordered crystallites simultaneously causing the residual UCl_4 to recrystallize in the form of larger and more perfect crystals.

Infra-red spectrophotograms of solid $UCl_4 \cdot 4n\text{-}C_3H_7NH_2$, solid UCl_4 and liquid $n\text{-}C_3H_7NH_2$ by means of the KBr disc method and also of gaseous $n\text{-}C_3H_7NH_2$ in a 10 cm gas cell were taken. The absorption peaks observed on $n\text{-}C_3H_7NH_2$ by the two above methods were essentially identical, except for some irregular shifts in the region of 900 cm^{-1} to 1100 cm^{-1}. In the spectrum of the addition compound all C–H and N–H stretching frequencies were extremely broadened with respect to the same frequencies in the components; the whole region from 2700 cm^{-1} to 3500 cm^{-1} had become highly absorbing. The above, to a lesser degree, was also true for the C–H and the N–H bending frequencies at 1470 cm^{-1} and 1620 cm^{-1}, respectively, which now

[12] R. C. L. MOONEY, *Acta Cryst.* **2**, 191 (1949).

occupied a broad region from 1450 cm^{-1} to 1650 cm^{-1}. Some new prominent peaks were observed in the spectrum of the addition compound which were not seen in the component spectra under identical experimental conditions. Their positions were at 900 $\pm$ 30 cm^{-1}, 1180 $\pm$ 10 cm^{-1}, 1950 $\pm$ 50 cm^{-1}, 2500 $\pm$ 30 cm^{-1}, 2600 $\pm$ 30 cm^{-1}, 2670 $\pm$ 30 cm^{-1}. The latter three overlapped. These observed peaks could not be assigned to any specific U–N bonding, since it was not known in what infra-red region the appropriate stretching or bending frequencies would fall. One may say, that the bond strengths in the addition compound differ significantly from the bond strengths observed in the components.

All of the systems investigated react with gaseous H_2O at room temperature. The sensitivity toward traces of H_2O seemed to increase with increasing mole ratio of ligand. The reaction equations proposed for the addition compounds are,

$$\underset{(s)}{UCl_4 \cdot 6N_2H_4} + \underset{(g)}{2H_2O} \rightarrow \underset{(s)}{UO_2} + \underset{}{4N_2H_5Cl} + \underset{(l)}{2N_2H_4},$$

and

$$\underset{(s)}{UCl_4 \cdot 4RNH_2} + \underset{(g)}{2H_2O} \rightarrow \underset{(s)}{UO_2} + \underset{(s)}{4RNH_3Cl}$$

These reactions went to completion when a sufficient quantity of H_2O was available. The presence of solid UO_2 and ligand hydrochloride was confirmed by X-ray analysis. Basic U(IV) chlorides, for example $UCl_3(OH)$, may have been intermediates in the above reactions, but they were not observed in the reaction products.

Standard enthalpies and free energies of reaction at 25° were calculated for the reaction,

$$\underset{(s)}{UCl_4} + \underset{(l)}{4N_2H_4} + \underset{}{2H_2O} \rightarrow \underset{(s)}{UO_2} + \underset{(s)}{4N_2H_5Cl};$$

$\Delta H^\circ = -126$ kcal/mole and $\Delta F^\circ = -147$ kcal/mole, and

$$\underset{(s)}{UCl_4} + \underset{(g)}{4CH_3NH_2} + \underset{(g)}{2H_2O} \rightarrow \underset{(s)}{UO_2} + \underset{(s)}{4CH_3NH_3Cl};$$

$\Delta H^\circ = -154$ kcal/mole and $\Delta F^\circ = -89$ kcal/mole.

For the imaginary reaction,

$$\underset{(s)}{UCl_4} + \underset{(g)}{2H_2O} \rightarrow \underset{(s)}{UO_2} + \underset{(g)}{4HCl};$$

$\Delta H^\circ = +22$ kcal/mole and $\Delta F^\circ = +3$ kcal/mole.

The data required for the above computations are found in references.[13–17] The very large negative ΔH° and ΔF° values agree with the extreme instability toward traces of water vapour at room temperature.

The reaction of UCl_4–NH_3 systems with H_2O was not investigated. It was noted,

[13] J. J. KATZ and E. RABINOWITCH, *loc. cit.*, pp. 295, 297, 483.
[14] E. GREENBERG and E. F. WESTRUM JR., *J. Amer. chem. Soc.* **78**, 4526 (1956).
[15] L. F. AUDRIETH and B. ACKERSON OGG, *loc. cit.*, pp. 76, 80.
[16] *Selected Chemical Thermodynamic Properties*, N. B. S. Circular 500, U. S. Government Printing Office, Washington, D.C. (1952).
[17] J. G. ASTON, *J. Amer. chem. Soc.* **68**, 1415 (1946); **76**, 4492 (1954).

however, that the dark brown $UCl_4 \cdot 2NH_3$ when exposed to atmospheric moisture turned green in colour within 15 min. For the reaction at 25°,

$$\underset{(s)}{UCl_4} + \underset{(g)}{4NH_3} + \underset{(g)}{2H_2O} \rightarrow \underset{(g)}{UO_2} + \underset{(s)}{4NH_4Cl},$$

by calculation $\Delta H^\circ = -148$ kcal/mole and $\Delta F^\circ = -85$ kcal/mole.

All of the systems react with dry O_2 at room temperature at or below the partial pressure of O_2 in the atmosphere. For the UCl_4–N_2H_4 the reaction appeared to proceed in two steps. The first reaction seemed to be,

$$\underset{(s)}{UCl_4 \cdot 6N_2H_4} + \underset{(s)}{3/2O_2} \rightarrow \underset{(s)}{UO_2Cl_2} + \underset{(s)}{2N_2H_5Cl} + \underset{(g)}{N_2} + \underset{(l)}{3N_2H_4} + \underset{(l)}{H_2O}.$$

The UO_2Cl_2 and N_2H_5Cl were identified by means of X-ray analysis. The stoicheiometry was not definitely established because the products reacted further to give UO_2, N_2H_5Cl and non-condensable gas or gases, in addition to the O_2 already present. These gases could only be N_2 and possibly, H_2. The most likely overall reaction seemed to be,

$$UCl_4 \cdot 6N_2H_4 + 2O_2 \rightarrow UO_2 + 4N_2H_5Cl + 2N_2 + 2H_2O.$$

By calculation, $\Delta H^\circ = -382$ kcal/mole and $\Delta F^\circ = -365$ kcal/mole for this reaction at 25° Analysis of the products showed that in the final product the mole ratio of hydrazine mono-hydrochloride to uranium was close to four. Hydrazine dihydrochloride was not found in the products.

In the UCl_4–amine systems the reaction was a little less sensitive toward oxygen than the UCl_4–N_2H_4 one. Only UO_2Cl_2 and the amine hydrochloride were found in the solid product. Evidently the reaction,

$$UO_2Cl_2 + m\ RNH_2 \rightarrow UO_2 + 2RNH_3Cl + \text{polymer},$$

to be described in a following paper, proceeded at too slow a rate to be observed, probably because of lack of free amine. The kinetics of reaction between solid UCl_4 and gaseous O_2 has been reported in the literature.[18] The reaction, $UCl_4 + O_2 \rightarrow UO_2Cl_2 + Cl_2$, was observed to start at a measurable rate at $230° \pm 5°$ at which temperature the activation energy is approximately 12 ± 2 kcal/mole. In the present work the reaction occurred at a measurable rate at 25° and oxygen pressures as low as 20 mm. The rate depended on the quantity of amine present in the solid UCl_4–RNH_2 system—the more amine present, the higher the rate of oxidation. As a matter of fact, UCl_4 was oxidized even more rapidly when dissolved in excess anhydrous liquid amine in the presence of atmospheric oxygen. Within a few hours the solution had changed in colour from nearly black to orange indicating the oxidation of solvated U(IV) ions to solvated UO_2 (II) ions.

The oxidation of UCl_4–NH_3 systems was not investigated extensively. Some qualitative observations indicate that the solid oxidation products correspond to those obtained in the oxidation of UCl_4–RNH_2 systems.

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J. Inorg. Nucl. Chem., 1958, Vol. 7, pp. 66 to 72. Pergamon Press Ltd., London

THE INTERACTION OF AMMONIUM AND POTASSIUM HEXABROMOÖSMATE(IV) AND LIQUID AMMONIA AT −34 AND 90°*

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Abstract—The reactions that occur slowly at −34° are shown to lead to complex mixtures of ammonia-insoluble and ammonia-soluble products of reactions that include ammonolysis are and therefore controlled by amide ion concentration. Reactions of the ammonia-insoluble products with 48% hydrobromic acid, saturated silver sulphate solution, and gaseous ammonia are described. The ammonia-insoluble products include hexammineosmium(III) hexabromoösmate(III). Ammonia-soluble mixtures formed at −34° could not be resolved; they consisted of diamagnetic osmium compounds in which the Os : Br ratios approached 1 : 2·00. Reactions at 90° yield only ammonia-soluble products consisting of μ-nitridobis[dibromo-tetrammineosmium(IV)] bromide and hexammineosmium(III) bromide together with lesser quantities of other diamagnetic and paramagnetic osmium complexes.

IT is shown elsewhere[1,2] that the reaction between the bromoösmate(IV) ion and liquid ammonia at 25° yields ammonia-insoluble hexammineosmium(III) hexabromoösmate(III) and the ammonia-soluble binuclear complex, μ-nitridobis [dibromotetrammineosmium(IV)] bromide. These products predominate despite rather considerable variation in the conditions of reaction. In contrast, results reported in the present paper show that the same reactants at −34° yield practically intractable mixtures of osmium complexes; at 90° mixtures also are formed, but the results obtained are reasonable in relation to the reactions known to occur at 25°.

Because so many of the reactions studied at −34 and 90° failed to lead to conclusive results in the sense of isolation of pure products, only representative data are reported here. Ranges of reaction conditions are specified and the gross characteristics of the reaction products are described; the more detailed data are recorded elsewhere.[3] Nevertheless, the data given below serve both to indicate the over-all character of the reaction products and to emphasize their extreme complexity.

EXPERIMENTAL

With the following exception, all materials and methods were the same as those described previously.[1,2,4] Reactions at −34° were carried out using equipment of the type described by WATT and MOORE.[5]

Reactions at −34°

In a typical experiment, 70 ml of anhydrous liquid ammonia was condensed on 1·0477 g (1·4 mmole) of K_2OsBr_6 at −38° over a period of 1·5 hr. The temperature was increased to −34° and the volume of solution was maintained essentially constant for a total contact time of 27 hr. At the end of the first 2 hr, orange to brown coloured crystals began to separate from the red solution. The separation of massive

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[1] G. W. WATT and L. VASKA, *J. Inorg. Nucl. Chem.* **5**, 304 (1958).
[2] G. W. WATT and L. VASKA, *J. Inorg. Nucl. Chem.* **5**, 308 (1958).
[3] L. VASKA, *Dissertation*, The University of Texas, (1956).
[4] G. W. WATT and L. VASKA, *J. Inorg. Nucl. Chem.* **6**, 246 (1958).
[5] G. W. WATT and T. E. MOORE, *J. Amer. chem. Soc.* **70**, 1197 (1948).

and apparently homogeneous brown crystals continued while the intensity of coloration of the ammonia solution progressively decreased to a pale pink colour after 25 hr. Finally over a period of 3 hr, the reaction mixture was filtered, the brown crystals were washed six times with 25 ml portions of ammonia, and the colourless washings were combined with the filtrate. Following evaporation of the solvent, the ammonia-soluble products were treated as described below.

Essentially the same observations were recorded for runs employing either $(NH_4)_2OsBr_6$, or K_2OsBr_6 in the presence of added NH_4Br.

Ammonia-insoluble products. Residual ammonia was removed from the insoluble product at room temperature and 10^{-3} mm for 10 hr; the solid was stored in a nitrogen atmosphere under anhydrous conditions. (Found: Os, 42·6; Br, 41·8; Os : Br, 1: 2·31). The yield based on osmium was 70 per cent and the magnetic susceptibility per gram ($\chi_g \times 10^6$) was 1·7. The X-ray diffraction pattern for this product led to the following interplanar spacings (d, Å); relative intensities are given in parentheses: 7·5 (0·1), 6·0 (1·0), 5·26 (0·1), 4·29 (0·1), 3·82 (0·1), 2·90 (0·1), 2·69 (0·1).

Similar products (and the corresponding ammonia-soluble products) were obtained from reactions carried out using the following ranges of conditions: Approximate initial concentration of $(OsBr_6)^{2-}$ (i.e. after completion of condensation of ammonia), 0·016 to 0·132 mole/l.; concentration of NH_4^+, 0 to 1·862 moles/l.; time, 23 to 57 hr.* The yields of ammonia-insoluble products (based on osmium) ranged from 36 to 86 per cent; the osmium content from 40·2 to 46·2 per cent; the bromine content from 39·0 to 49·1 per cent and (based on fewer data), the nitrogen content ranged from 9·99 to 13·3 per cent. The osmium to bromine ratios ranged from 1 : 2·02 to 1 : 2·91† and the magnetic susceptibility per gram ranged from 1·1 to 1·7. The X-ray diffraction patterns for these products all revealed spacings clearly attributable to hexammineosmium(III) hexabromoösmate(III)[1] together with others that could not be accounted for in terms of data for known osmium compounds.

The ranges of composition given above imply the formation of mixtures despite the apparent homogeneity of the brown crystalline ammonia-insoluble product. A detailed examination of the available data, however, shows that the principal controlling variable (assuming virtually complete reaction) is the concentration of ammonium ion that is either generated *in situ* (by the ammonolysis of $OsBr_6^{2-}$ or by ligand substitution) and/or added initially as $(NH_4)_2OsBr_6$ and/or NH_4Br. This conclusion is supported by the experiments described below.

That the formation of hexammineosmium(III) hexabromoösmate(III) is favoured by the presence of appreciable concentrations of ammonium ion may be seen from the results of two specific experiments (7A and 17A), both of which involved $(NH_4)_2OsBr_6$ and a reaction time of 57 hr. In run 7A, 1·4066 g of $(NH_4)_2OsBr_6$ was used, while in run 17A, 2·7912 g of $(NH_4)_2OsBr_6$ and 4·699 g of NH_4Br were employed. The data relating to the two ammonia-insoluble products are given in Table 1.

The predominance of products involving osmium to bromine ratios that approach 1 : 2·00 when shorter reaction times and relatively low potential ammonium ion concentrations prevail is demonstrated by the following experiment. In run 2,

* Data on products of reactions over much shorter times ($\leq$2·5 hr) indicate quite incomplete reactions; for example, the corresponding yields of ammonia-insoluble products were $\leq$11 per cent.

† Lower Os : Br ratios were found when K_2OsBr_6 (only) was used and the total reaction time was relatively short. For example, for a reaction time of 1·5 hr, the Os : Br ratio found was 1 : 1·74.

0·8016 g of K_2OsBr_6 was allowed to react with liquid ammonia at −34° for 26 hr. The yield of ammonia-insoluble product was 41 per cent. (Found: Os, 45·2; Br, 39·0; N, 13·3; Os : Br, 1 : 2·05. Calc. for $[Os(NH_3)_2(NH_2)_2Br_2]$: Os, 45·7; Br, 38·4; N, 13·5.)

TABLE 1.—DATA FOR AMMONIA-INSOLUBLE PRODUCTS FROM REACTIONS AT −34°

Run No.	Found*			
	Os (%)	Br (%)	Os : Br	Yield (%)
7A	40·9	44·8	1 : 2·61	74
17A	40·2	49·1	1 : 2·91	47

* Calc. for $[Os(NH_3)_6](OsBr)_6$:
Os, 39·5; Br, 49·8; Os : Br, 1 : 3·00.

Reactions of ammonia-insoluble products. In an extensive series of experiments,[3] reactions of different ammonia-insoluble products of reactions at −34° with 48% HBr were studied under a variety of conditions. The results were largely unsatisfactory in that mixtures of osmium complexes were almost invariably found to comprise both the acid-insoluble and the acid-soluble products. However, X-ray diffraction, magnetic susceptibility, and analytical data for several such products did serve further to establish the presence of (HBr-insoluble) hexammineosmium(III) hexabromoösmate(III) as a major component of ammonia-insoluble products formed under conditions of relatively high ammonium ion concentration. Several different products were isolated from the soluble fractions resulting from the treatment with HBr. Complete characterization of these products was not accomplished in some cases owing to the extremely small quantities available following repeated recrystallization. Nevertheless, the results given in Table 2 are representative and serve to show the nature of these products.

The behaviour of these ammonia-insoluble products toward gaseous ammonia at elevated temperatures was found to be dependent upon the conditions that prevailed in the initial reactions with liquid ammonia. Products for which the Os : Br ratio was relatively low (i.e. approaching 1 : 2·00) were reduced to elemental osmium without visual evidence of intermediation of other entities. For cases corresponding to the higher Os : Br ratios, however, the following example is typical. A sample (0·6583 g) of a product in which the Os : Br ratio was 1 : 2·51 was exposed to a stream of ammonia gas and heated up to 280° over a period of 8 hr; a brown solid was formed. The temperature was lowered to 260°, the exposure to ammonia gas was continued for 10 hr, and the solid product was cooled to room temperature in a helium atmosphere. This product dissolved completely in 15 ml of water acidified with one drop of 48% HBr. Further addition of a few milliliters of 48% HBr and 40 ml of ethyl alcohol followed by cooling to 0° resulted in the separation of a tan coloured solid that was filtered, washed with absolute alcohol, and dried under reduced pressure over $Mg(ClO_4)_2$. The yield was 0·4555 g or 68 per cent based on osmium. (Found: Os, 40·2; Br, 42·4; N, 12·8; μ, 1·1 B.M. based on one-half the molecular weight of the binuclear complex specified. Calc. for $[Os_2(NH_3)_8NBr_2]Br_3$: Os, 40·9; Br, 42·95; N, 13·6.) A sample of this bromide was converted to the iodide

TABLE 2.—SOLUBLE PRODUCTS FROM REACTIONS WITH HYDROBROMIC ACID

Initial Os : Br[b]	Products isolated[a]		
	Os (%)	Br (%)	Os : Br
1 : 2·05	37·7	46·7	1 : 2·95[c]
1 : 2·28	37·8	46·5	1 : 2·93
1 : 2·51	39·5	41·8	1 : 2·51[d]
1 : 2·51	39·2	40·9	1 : 2·49[d]
1 : 2·51	36·5	45·4	1 : 2·96[e]
1 : 2·61	36·7	47·8	1 : 3·10
1 : 2·91	37·2	46·5	1 : 2·98[f]

[a] Calc. for:

	Os (%)	Br (%)
$[Os(NH_3)_4Br_2]Br{\cdot}H_2O$	36·9	46·5
$[Os(NH_3)_5Br]Br_2$	36·9	46·5
$[Os(NH_3)_5Br]Br_2{\cdot}H_2O$	35·7	45·0
$[Os(NH_3)_4]Br_3$	35·7	45·1
$[Os_2(NH_3)_8NBr_2]Br_3{\cdot}2H_2O$	39·4	41·4
$[Os_2(NH_3)_8NBr_2]Br_3{\cdot}3H_2O$	38·6	40·6

[b] I.e. the initial ammonia-insoluble product that was treated with HBr.
[c] Found: N, 10·8. Calc. for $[Os(NH_3)_4Br_2]Br{\cdot}H_2O$: N, 10·9.
[d] Diamagnetic. [e] μ = 2·0 B.M. [f] μ = 1·9 B.M.

by dissolution in the minimum quantity of water, addition of hydriodic acid and ethanol, and isolation as described for the bromide. (Found: Os, 35·2; N, 11·8. Calc. for $[Os_2(NH_3)_8NBr_2]I_3$: Os, 35·5; N, 11·8.) The yellow-brown iodide was essentially diamagnetic. Another sample of the bromide was converted to the brown diamagnetic chloride by an entirely analogous procedure. (Found: Os, 47·2; N, 16·2. Calc. for $[Os_2(NH_3)_8NBr_2]Cl_3$: Os, 47·7; N, 15·8.) Although neither the bromide nor iodide gave a satisfactory X-ray diffraction pattern, a good pattern was obtained for the chloride; the data are given in Table 3.

Reactions of the ammonia-insoluble products with saturated silver sulphate solution[1] also led to soluble and insoluble products that consisted of complex mixtures. Although analytical data[3] for most of the insoluble fractions were not conclusive *per se*, such data together with X-ray diffraction patterns established the

TABLE 3.—X-RAY DIFFRACTION DATA FOR μ-NITRIDOBIS-[DIBROMOTETRAMMINEOSMIUM(IV)] CHLORIDE

d, Å	I/I_o	d, Å	I/I_o
7·8	0·40	3·87	0·60
6·7	0·80	3·74	0·40
5·8	0·80	3·48	0·05
5·32	1·00	3·35	0·05
4·91	0·05	3·16	0·10
4·51	0·05	2·77	0·05
4·19	0·10	2·68	0·40

presence of impure hexammineosmium(III) bromide and silver(I) hexabromoösmate (IV) as reaction products. Thus, these data serve further to establish the presence of hexammineosmium(III) hexabromoösmate(III) as a major component of the ammonia-insoluble products. The following are examples of results obtained in efforts to identify products present in the soluble fractions from treatment of ammonia-insoluble products with saturated silver sulphate solution. An ammonia-insoluble product having an Os : Br ratio of 1 : 1·74 was treated with silver sulphate solution; an orange-coloured solid was isolated from the soluble fraction by procedures that are described in detail elsewhere.[3] (Found: Os, 51·1; Br, 21·0. Calc. for $[Os(NH_3)_4(OH)_2]Br$: Os, 51·2; Br, 21·5.) Similarly, for a case in which the initial Os : Br ratio was 1 : 2·51, treatment of the soluble fraction with HI provided a yellow solid. (Found: Os, 46·1; N, 14·0, μ, 1·8 B.M., Calc. for $[Os(NH_3)_4(OH)_2]I$: Os, 45·4; N, 13·4.) The X-ray diffraction pattern for this product led to the following data (d, Å; relative intensities in parentheses); 6·9 (0·3), 6·1 (0·8), 5·33 (0·5), 5·00 (0·5), 4·00 (1·0), 3·76 (0·8).

Ammonia-soluble products. Upon completion of reactions at −34° as described above, evaporation of the solvent from the combined supernatant solution and washings yielded a mixture of white and intensely green coloured crystals. Separation of the white crystals (NH_4Br and/or KBr) was effected by leaching with absolute alcohol,[2] but extensive studies failed to establish the identity of the species that comprised the green solid. The only conclusion that could be reached was that a major component was an osmium complex in which the osmium to bromide ratio was 1 : 2·00; some of the data were strongly indicative of the presence of $[Os(NH_3)_4]Br_2$.[3]

Reactions at 90°

These reactions were carried out in the manner described previously.[1] In a typical case, 1·9287 g of $(NH_4)_2OsBr_6$ in 40 ml of liquid ammonia was heated slowly from −75 to 90°, maintained at the latter temperature for 1 hr, then cooled to room temperature over 14 hr. The reaction mixture consisted of an intensely yellow to brown coloured ammonia solution; there was no ammonia-insoluble product. Evaporation of the solvent left a mixture of yellow-tan crystals and white crystals of NH_4Br which was removed by extraction with absolute alcohol.[2] The tan solid was dried *in vacuo*. (Found: Os, 37·7; Br, 42·1; Os : Br, 1 : 2·65; magnetic susceptibility per gram ($\chi_g \times 10^6$), 1·2.) It is at once apparent that the overall characteristics of this product are similar to those of the ammonia-soluble products from the corresponding reactions at 25°.

Accordingly, the tan solid was subjected to fractional dissolution in dilute HBr;[2] seven different small fractions of solid products were thus isolated.[3] In the order of increasing solubility of these products, the osmium content decreased from 39·2 to 37·1 per cent, while the bromine content increased from 35·9 to 43·5 per cent; the Os : Br ratios increased from 1 : 2·18 to 1 : 2·79. The least soluble fractions were diamagnetic; among the more soluble fractions the paramagnetic susceptibility increased progressively with increasing solubility.

One of the less soluble but intermediate fractions was found to consist (in reasonable purity) of the diamagnetic binuclear complex previously described.[2] (Found: Os, 38·3; Br, 40·2. Calc. for $[Os_2(NH_3)_8NBr_2]Br_3 \cdot 3H_2O$: Os, 38·6;

Br, 40·6.) Similarly, one of the more soluble and paramagnetic products was found to consist of impure hexammineosmium(III) bromide which was purified by conversion to the iodide.[2] (Found: N, 12·4. Calc. for $[Os(NH_3)_6]I_3$: N, 12·5.) The magnetic susceptibility based on the formula given corresponded to 1·5 B.M.; this product gave an X-ray diffraction pattern identical with that reported elsewhere.[1] The least soluble fraction isolated in the course of these experiments is of interest since it may be a case in which osmium exhibits coordination number eight. This gray-tan solid was diamagnetic, and although a pure product was not obtained, the elemental composition found corresponded most closely to the formula $[Os(NH_3)_4(NH_2)_4]Br_2$.

DISCUSSION

The studies described above, together with results not included here,[3] clearly indicate that the interaction of ammonium and potassium hexabromoösmate(IV) and liquid ammonia at −34° is much more complex than at 25°.[1,2] When K_2OsBr_6 is used, the ammonia-insoluble product consists largely of osmium complexes in which the osmium to bromine ratio approaches 1 : 2·00. The use of $(NH_4)_2OsBr_6$ either as such or in the presence of added NH_4Br, or K_2OsBr_6 plus NH_4Br tends however to produce ammonia-insoluble products in which the osmium to bromine ratio approaches 1 : 3·00. Although hexammineosmium(III) hexabromoösmate(III) was identified as a major component of the ammonia-insoluble product, this salt is not predominant as it is at 25°.

We believe that the factor primarily responsible for the differences noted above and for the overall complexity of these reactions is the concentration of amide ion. Thus, for the *initial* reaction between K_2OsBr_6 and liquid ammonia at −34°, the concentration of amide ion is relatively high and extensive ammonolysis apparently occurs over the long reaction times involved; this may be represented for the general case as follows, assuming that the 4^+ oxidation state of osmium is maintained,

$$(OsBr_6)^{2-} + (2z + n)NH_3 \rightarrow [Os(NH_3)_n(NH_2)_zBr_m] + zNH_4Br + 2Br^-$$

where $z + m = 4$; $z = 0,1,2,3,4$; $m = 0,1,2,3$; and $n = 0,1,2,3$. As ammonolysis proceeds, the concentration of ammonium ion increases; this suppresses the amide ion concentration and there obtains a condition similar to that in which ammonium ion is present initially at higher concentrations. This interpretation is supported not only by the data given above but also by the fact that, in the course of experiments not reported in detail here, products that approximated the compositions represented by the formulas $[Os(NH_3)_2(NH_2)_2Br_2]$ (i.e. $n = z = m = 2$) and $[Os(NH_3)_2(NH_2)Br_3]$ (i.e., $n = 2$, $z = 1$, $m = 3$) were isolated. The details relating to the latter product are not reported here because the analytical and other data are not considered sufficient for an unequivocal identification. Furthermore, the analytical data for some of the products formed in the early stages of reactions of K_2OsBr_6 suggest that even more extensive ammonolysis leading to products containing imido and possibly nitrido groups may have occurred. As the amide ion concentration decreases or is decreased initially by providing a high concentration of ammonium ion, the reactions that occur tend to approach those observed at 25°. This is reflected in the data given in Table 1; the relative yields in the two experiments in question demonstrate the extent to which the previously described conversion of hexammineosmium(III)

hexabromoösmate(III) to hexammineosmium(III) bromide occurs under conditions of high ammonium ion concentration (run 17A). Undoubtedly, the complexity of both the ammonia-soluble and ammonia-insoluble products formed at −34° is determined largely by the fact that several ammonolytic reactions of the type indicated above occur either simultaneously or consecutively. The resulting ammonolysis products have so many properties in common that their separation is understandably difficult.

While our studies of the reactions that occur at 90° were not extensive, it appears that these reactions are analogous to those that occur over longer periods at 25°.[1,2] The principal osmium compound isolated was μ-nitridobis[dibromotetrammineosmium(IV)] bromide. The absence of an ammonia-insoluble product is probably attributable to the formation of hexammineosmium(III) hexabromoösmate(III) and (at the higher temperature) its rapid conversion to ammonia-soluble hexammineosmium(III) bromide and ammonium hexabromoösmate(IV) in the manner previously described.[1] The former product was isolated as the iodide; the latter was not isolated, but its presence in solid products was evidenced by X-ray diffraction patterns and its presence in solution was undoubtedly responsible for the characteristically intensely coloured solutions observed.

Finally, it should be emphasized that most of the solids separated from products of reactions at 90° were rather complex mixtures; even reasonably pure compounds were separated only by tedious fractionation procedures.

Further results of studies on the lower oxidation states of osmium will be published in forthcoming publications from this laboratory.

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THE ABSORPTION SPECTRA OF COMPLEX SALTS—II
CUPRIC COMPLEXES WITH DECARBOXYLIC ACIDS

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Abstract—Complexes of cupric ion with the anions of oxalic, malonic and some substituted malonic acids have been studied in aqueous solution. The wavelength of the absorption band of the cupric ion in the red region of the visible spectrum remains almost constant throughout the entire series of complexes (about 700 mμ) but the extinction of this band increases as the size of the dicarboxylate ion increases and a linear relationship is shown to exist between the extinction and the molar refractivity (R_D) of the co-ordinated anion.

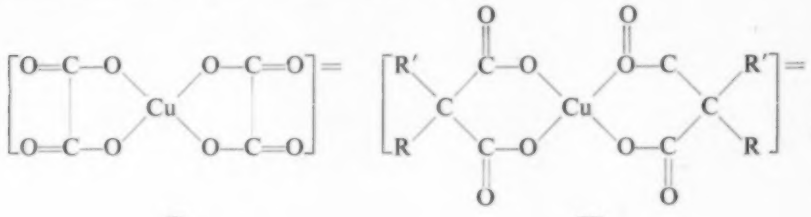
IN part I[1] the absorption spectra of a series of complex oxalates were studied and the absorption of the oxalate groups in the region of 250 mμ correlated with the properties of the metal cations to which they were co-ordinated. The present paper describes the effect on the absorption of a transition metal cation of varying the nature of the co-ordinated ligands when these are dicarboxylates forming 5–, 6–, or 7–membered chelate rings.

The long wavelength, low intensity absorption bands of transition metal compounds (particularly of manganese, cobalt, nickel and copper) are ascribed to localized transitions of the *d* electrons of the metal, these normally forbidden transitions being made possible by the effect of co-ordinated groups in removing the degeneracy of the *d*-orbitals. Changes in the enviroment of the metal atom may thus be expected to affect these low intensity absorption bands. Some general conclusions can be drawn from published data; for example the absorption of cupric ions appears to take place at shorter wavelengths in a more basic environment (compare the absorption of $Cu.aq.^{++}$ and $Cu(NH_3)_4^{++}$) and the absorption of nickel ions seems to be similarly affected; in the series of 4–co-ordinated platinous complexes $[Pt(NH_3)_nCl_{4-n}]^{(n-2)+}$, the replacement of Cl^- by NH_3 results at each step in the movement of the absorption bands to shorter wavelengths.[2]

In studying these effects it is preferable that the absorption of the metal atom should be free from interference by other absorbing species and that its environment should be controllable with certainty as by the formation of stable complexes. For these reasons cupric ion was chosen, the absorption band being at long wavelength (550–800 mμ) and the complexes comparatively stable. Even so the range of complexes highly stable in aqueous solution is small and mainly confined to those stabilized by

[1] D. P. GRADDON, *J. Inorg. Nucl. Chem.* **3**, 308 (1956).
[2] J. CHATT, G. A. GAMLEN and L. E. ORGEL, *J. Chem. Soc.* 486 (1958).

chelation of which one of the simplest series is formed by the complex dicarboxylates, such as cuprioxalates (I) and cuprimalonates (II):—



(I) (II)

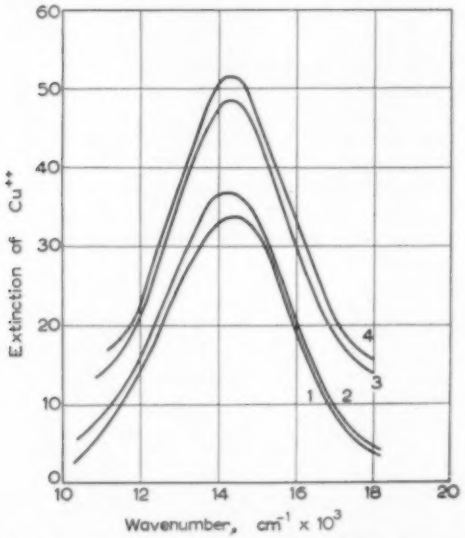


FIG. 1.—Absorption curves of cuprioxalate (1) cuprimalonate (2) cuprimethymalonate (3) and cupriethylmalonate (4) anions.

These complexes are readily formed by the addition of an excess of potassium oxalate or malonate to cupric sulphate solutions. From the resulting deep blue solutions, salts such as $K_2[Cu(C_2O_4)_2]2H_2O$ and $K_2[Cu(CH_2C_2O_4)_2]2H_2O$ can be obtained and as the light absorption changes no further when the excess of the potassium dicarboxylate exceeds about 2½-fold, they clearly contain these complex ions. Substituted malonates behave similarly except that when the substituents are large a greater excess of the potassium salt is needed to complete the complex formation, and with the phenylmalonate, phenylmethylmalonate and butylethylmalonate the intermediate neutral cupric salt is only sparingly soluble but redissolves in excess of the potassium salt (as occurs also with the oxalate); in these three cases complex formation is incomplete even with large excesses of the potassium salts and the absorption of the complexes must be obtained by extrapolation.

Fig. 1 shows some typical absorption curves, which are almost perfect Gaussian curves and can fairly be regarded as representing single electronic transitions as is required by crystal field theory for the tetragonally co-ordinated cupric ion.[3]

[3] J. BJERRUM, C. J. BALLHAUSEN and C. K. JØRGENSEN, *Acta chem. Scand.* **8**, 1275 (1954).

Table 1 shows the wavelengths and molar extinctions of the low intensity absorption band of the cupric ion for a series of these complexes, giving for comparison the absorption of the cupric-ethylenediamine ion and aqueous cupric sulphate, the concentration of the cupric ion being 0·01 molar throughout.

Owing to the breadth of the peaks the wavelengths recorded in the table are subject to an experimental error of about ± 5 mμ and as all but three fall in the range 690–710 mμ it appears that the energy of the electronic transition is not materially affected by changes in the ligand despite the wide range of acidity of the corresponding dicarboxylic acids. It may be significant that the absorption occurs at measurably shorter wavelength with the two dialkyl-substituted malonates in which the malonate

TABLE 1.—ABSORPTION OF CUPRIC DICARBOXYLATE COMPLEXES

	Dicarboxylate ion	λ (mμ)	ε
1	Oxalate	700	33·5
2	Malonate	700	36·6
3	Methylmalonate	695	48·3
4	Ethylmalonate	700	51·1
5	*n*-Propylmalonate	697	47·5
6	*n*-Butylmalonate	695	55·4
7	Diethylmalonate	680	58·4
8	Ethyl-*n*-butylmalonate	680	69*
9	Phenylmalonate	690	61*
10	Phenyl-methylmalonate	710	69*
11	Chloromalonate	720	40·9
12	Bromomalonate	710	41·8
13	Dibromomalonate	705	40·3
14	Phthalate	690	73·5*
	Cupric ethylenediamine	550	64
	Cupric sulphate	800	11·8

* Extrapolated values.

ion would be expected to have the highest polarizability and at measurably longer wavelength in the chloromalonate in agreement with the general trend noted above.

The extinction however increases from about 33·5 in the oxalate to about 70 in the phthalate and highly substituted malonates. The increase is evidently related to the size of the co-ordinated anion, a linear relationship being observed between the extinction and the molar volume properties of the ligand. Of the various forms of the molar volume the best straight line is obtained by plotting the molar refractivities (R_D) against the extinction (Fig. 2). On the graph the values of R_D are those obtained by adding the mean refraction equivalents of the components of one ligand anion. The obedience of the phenyl- and halogen- substituted malonates to this relationship is clear evidence that electronic and inductive effects are of very small importance, though the low extinction of the dibromomalonate suggests that these effects may play some part in extreme cases, but this may be due to distortion of the chelate ring.

The linear relationship between the molar volume of the ligand and the extinction of the cupric ion absorption band is less well satisfied by the acids which form 7–membered chelate rings. These acids, as might be expected, form much less stable

complexes. The absorption of the cupri-phthalate ion has been determined by calculated extrapolation;[4] the unstable maleate complex has an extinction of about 60 at a wavelength of about 680 mμ and the succinate complex is so unstable that cupric succinate is only soluble in nearly saturated solutions of potassium succinate. The change in environment caused by formation of the relatively unstable 7–membered ring thus has considerable effect and the relationship between molar volume and extinction must be considered as being restricted to the complexes containing 5– and 6–membered rings. The complex carbonate, also stable only in very strong alkali carbonate solutions, presumably contains 4–membered rings and also has an abnormally high extinction (greater than 75 at a wavelength less than 695 mμ). Comparison

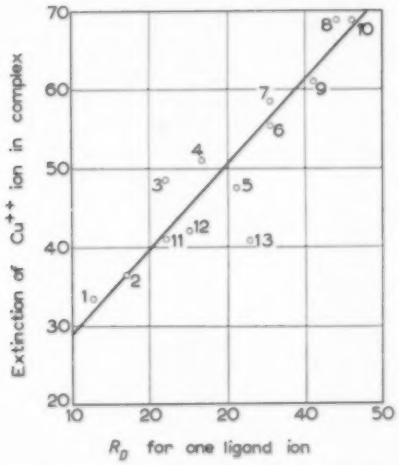


FIG. 2.—Relationship of extinction of Cu^{++} band to refraction equivalent of ligand. Ligands are numbered by reference to Table 1.

with aqueous cupric sulphate and cupric ethylenediamine indicates that the relationship cannot be generalized over a range of different types of ligand and can only be observed when the immediate environment of the cupric ion remains unchanged.

Most comparative spectroscopic studies have been devoted to the effects of conjugation or aromatic substitution and there are few examples which might be expected to show a similar effect of molar volume on a simple chromophore. In the simple aliphatic ketones however there is a general upward drift in the extinctions of the carbonyl absorption band as the size of the alkyl groups increases, accompanied by a slight variation in wavelength. Comparisons with other published data suggest however that this correlation is not of wide application.[5]

In the case of absorption in solution the physical significance of the extinction coefficient is not understood with precision. A few very complicated molecules show an extinction approaching the theoretical maximum of about 100,000 but when the extinction is very much smaller than this it must represent the probability of an electronic transition taking place when the chromophore is irradiated with light of suitable

[4] D. P. GRADDON, *J. Inorg. Nucl. Chem.* **5**, 219 (1958).
[5] Numerous tables are given by GILLAM and STERN, *An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry*. Arnold, London (1954).

energy. The present work thus indicates that the probability of a localized electronic transition taking place in the central atom of a complex ion is directly related to the molar volume of the ligands and hence to the size of the complex as a whole, provided that the immediate environment of the central atom is unchanged. This suggests that the outlying part of the complex is able to act as a light concentrating region and it is possibly significant that of the various forms of the molar volume the most satisfactory correlation with the extinction is given by the refraction equivalents.

EXPERIMENTAL

The potassium salts of substituted malonic acids were prepared by hydrolysis of the ethyl esters with ethyl alcoholic potassium hydroxide and their purity confirmed by gravimetric estimation of the potassium as potassium sulphate after fuming off organic matter with concentrated sulphuric acid.

Absorption spectra were determined on a Unicam SP500 spectrophotometer using glass cells of 1 cm path.

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KINETICS AND MECHANISM OF SUBSTITUTION IN COMPLEXES OF PALLADIUM(II)

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Abstract—The successive rates of substitution of acid groups (Cl, NO_2) in *trans*-dichlorodiammine-palladium(II), dichloroethylenediaminepalladium(II), *cis*- and *trans*-dinitrodiamminepalladium(II) by a variety of reagents of widely different nucleophilic character like water, aniline, glycine, pyridine, thiourea, and hydroxide ion were fully investigated by following the change in conductance of the solutions with time. The results indicated that the reactions are of the S_N2 type and the rates decrease in the following sequence of the incoming groups:

hydroxide ion > thiourea > pyridine > glycine > aniline > water.

This is also more or less the (decreasing) order of nucleophilic character of these groups.

The great dependence of the rate on the nucleophilic character of the incoming group, coupled with the fact that the *cis*-form was usually found to react faster than the corresponding *trans*-compound, indicates that the *trans*-effect is of no significance in the complexes of palladium(II). Moreover, the fact that *trans*-dinitrodiamminepalladium(II) reacts much more slowly than the corresponding dichloro complex shows that π-bonding activation of the *trans* position does not occur in these complexes.

THE *trans*-effect in platinum(II) complexes has been well-established[1] and several different theories have been advanced[2] to account for this phenomenon. Palladium-(II) resembles platinum(II) in forming an analogous series of complexes and the *trans*-effect might, therefore, be expected to lead to stereospecific substitutions in palladium complexes as in their platinum analogues. MANN *et al.*,[3] however, reported a complete reversal of Chernyaev's *trans*-elimination rule in the reaction of tetramminepalladium(II) ion with nitrite. JONASSEN and CULL[4] have proposed a roundabout mechanism, in line with the *trans*-elimination rule, to account for the reactions of some complexes of palladium(II). CHATT *et al.*,[5,6] and ORGEL[7] have developed a theory which correlates the *trans*-directing property of a group to its π-bonding character. This has been amply justified by the results of investigations carried out by ZVYAGINTSEV and KARANDASHEVA,[8] and BANERJEA *et al.*[9] CHATT has further pointed out[6] that conditions are more favourable for π-bonding in

[1] I. I. CHERNYAEV, *Ann. Inst. Platine Léningr.* **4**, 243,261 (1926); J. V. QUAGLIANO and L. SCHUBERT, *Chem. Rev.* **50**, 201 (1952).
[2] A. A. GRINBERG, *Ann. Inst. Platine, Léningr.* **10**, 58 (1932); *Acta physicochim. U.S.S.R.* **3**, 573 (1935); Y. K. SYRKIN, *Izv. Akad. Nauk. U.S.S.R.* (*otdel. Khim. Nauk*) **69** (1948); H. M. E. CARDWELL, *Chem. & Ind.* 422 (1955).
[3] F. G. MANN, D. CROWFOOT, D. C. GATTIKER and N. WOOSTER, *J. Chem. Soc.* 1642 (1935).
[4] H. B. JONASSEN and N. L. CULL, *J. Amer. Chem. Soc.* **73**, 274 (1951).
[5] J. CHATT, L. A. DUNCANSON and L. M. VENANZI, *Chem. & Ind.* 749 (1955).
[6] J. CHATT, L. A. DUNCANSON and L. M. VENANZI, *J. Chem. Soc.* 4456 (1955).
[7] L. E. ORGEL, *J. Inorg. Nucl. Chem.* **2**, 137 (1956).
[8] O. E. ZVYAGINTSEV and E. F. KARANDASHEVA, *Dokl. Akad. Nauk. SSSR* **101**, 93 (1955)
[9] D. BANERJEA, F. BASOLO and R. G. PEARSON, *J. Amer. Chem. Soc.* **79**, 4055 (1957).

platinum(II) than in any other similar element and, hence, the *trans*-effect cannot possibly be expected to be of great significance in the latter.

Furthermore, from qualitative observations reported in literature it appears that palladium(II) complexes are more labile than those of platinum(II). This seems to be justified by the ease of interconversion of the *cis*- and *trans*-forms, rapid transformation of the tetrammine into diacidodiammine by the action of acids, failure to get the mono- and tri-acido complexes, and in many other ways. TAUBE[10] has pointed out that qualitative observations on the reactivity of complexes are often misleading owing to the existence of equilibrium phenomena; even where rate data are available the degree of lability (i.e. the rate of substitution) may vary widely from one reagent to another owing to some specific influence of the incoming groups, as has been found by BANERJEA *et al.*[9] in the case of the complexes of platinum(II).

The present investigations were therefore undertaken in order to elucidate the factors which govern the rates of nucleophilic substitution in palladium(II) complexes, so as to have some quantitative idea of the relative labilities of the platinum(II) and palladium(II) systems under varying conditions, and to find out the occurrence or otherwise of the *trans*-effect phenomenon in the complexes of palladium(II).

The various complexes that have been investigated are *trans*-$Pd(NH_3)_2Cl_2$, $PdenCl_2$ (en = ethylenediamine), *cis*- and *trans*-$Pd(NH_3)_2(NO_2)_2$. The rates of liberation of both the acid groups successively by a wide variety of nucleophilic reagents like water, aniline, glycine, pyridine, thiourea, and hydroxide ion have been determined in aqueous solutions, at 36°C, by following the change in conductance with time.

EXPERIMENTAL

Preparation of materials

The complexes were prepared by following details given in the literature. These references and tests for each of the compounds are given below:

trans-Dichlorodiamminepalladium(II).[11] *Anal.* Calc: Pd, 50·42; N, 13·20. Found: Pd, 49·65; N, 13·72.

Dichloroethylenediaminepalladium(II).[11] *Anal.* Calc: Pd, 44·87. Found: Pd, 44·76.

trans-Dinitrodiamminepalladium(II).[3,4,12] The melting point is 231°C.

cis-Dinitrodiamminepalladium(II).[3,4,12] *Anal.* Calc: Pd, 45·95; N, 24·06. Found: Pd, 45·41; N, 24·29.

Determination of the rates of release of chloride or nitrite ions from the palladium(II) *complexes under the influence of water, aniline, glycine, pryidine, thiourea and hydroxide ion.*

These reactions have been studied by the conductance method following BANERJEA *et al.*[9] A Mullard Conductance Bridge was used for the purpose.

Since most of the reactions studied were rather fast, equimolar solutions of complex and reagent (each 0·0005 M) were studied in most cases. The order of the reaction was evaluated by plotting the data graphically using both the usual first- and second-order equations and noting which gave good agreement. From the slope the rate-constant was calculated as usual. Aquations were studied in 0·0005 M aqueous solutions of the complexes and rate-constants were evaluated graphically

[10] H. TAUBE, *Chem. Rev.* **50**, 69 (1952).
[11] H. D. K. DREW, F. W. PINKARD, G. H. PRESTON and W. WARDLAW, *J. Chem. Soc.* 1895 (1932).
[12] H. B. JONASSEN and T. O. SISTRUNK, *J. Phys. Chem.* **59**, 290 (1955).

TABLE 1.—(1) $Pd(en)Cl_2 + B \xrightarrow{k_1} Pd(en)BCl + Cl^-$

(2) *trans*-$Pd(NH_3)_2Cl_2 + B \xrightarrow{k_2}$ *trans*-$Pd(NH_3)_2BCl + Cl^-$

CONCENTRATION OF B and COMPLEX 0·0005 M. TEMP. 36°C

Incoming group B	Rate constants k or maximum time for change		Remarks	
	k_1	k_2	(1)	(2)
H_2O	Very fast	$2·3 \times 10^{-3}$ (min^{-1})	Reaction complete during dissolution	Complete
$C_6H_5·NH_2$	—	Fast (10 sec)	—	Complete
$H_2N·CH_2·CO_2H$	—	Fast (10 sec)	—	Complete
C_5H_5N	—	Fast (5 sec)	—	Complete
$SC(NH_2)_2$	—	Fast (5 sec)	—	Complete
OH^-	—	Fast (5 sec)	—	Complete

TABLE 2.—$Pd(en)(H_2O)Cl + B \xrightarrow{fast} Pd(en)BCl + H_2O$

(1) $Pd(en)BCl + B \xrightarrow{k_1} Pd(en)B_2 + Cl^-$

(2) *trans*-$Pd(NH_3)_2BCl + B \xrightarrow{k_2}$ *trans*-$Pd(NH_3)_2B_2 + Cl^-$

CONCENTRATION OF B AND COMPLEX 0·0005 M. TEMP. 36°C

Incoming group B	Rate constants k or maximum time for change		Remarks	
	k_1	k_2	(1)	(2)
H_2O	—	$7·3 \times 10^{-3}$ (min^{-1})	No reaction	Complete
$C_6H_5·NH_2$	Fast (5 sec)*	0·35 (l. $mole^{-1}$ min^{-1})	10% complete*	S_N2 Ca. 100% complete
$H_2N·CH_2·CO_2H$	0·39 (l. $mole^{-1}$ min^{-1})	1·9 (l. $mole^{-1}$ min^{-1})	See discussion	S_N2 Ca. 100% complete
C_5H_5N	Fast (5 sec)*	7·25 (l. $mole^{-1}$ min^{-1})	60% complete*	Complete
$SC(NH_2)_2$	Fast (5 sec)	Fast (5 sec)	Complete	Complete
OH^-	Fast (5 sec)	Fast (5 sec)	Complete	Complete

* Equilibrium is established in these cases. The reaction may be made to go to completion by using excess B, e.g. with a 0·0095 M solution of B.

using the first-order equation. This was also true for some of the reactions with aniline (cf. Table 4) where large excess of aniline could be used.

Some of the reactions were so fast that they were completed in a few seconds and in each of those cases the maximum observed time necessary for complete reaction or establishment of an equilibrium was evaluated.

In most of the cases the observed value of the final conductance (C_∞) agreed closely with that expected. Where it was not possible to get the experimental value of C_∞, due to decomposition, as in some of the reactions with aniline and thiourea,

TABLE 3.

(1) *cis*- $Pd(NH_3)_2(NO_2)_2 + B \xrightarrow{k}$ *cis*- $Pd(NH_3)_2BNO_2 + NO_2^-$
(2) *trans*- *trans*-

CONCENTRATION OF B AND COMPLEX 0·0005 M. TEMP. 36°C

Incoming group B	Rate constants or maximum time for change		Remarks	
	k_1	k_2	(1)	(2)
H_2O	Fast (10 min)*	Fast (10 min)*	40% complete*	40% complete*
$C_6H_5NH_2$	0·28 (l. mole^{-1} min^{-1})	0·93 (l. mole^{-1} min^{-1})	S_N2 70% complete	S_N2; yellow precipitate in 24 hr
$H_2N{\cdot}CH_2{\cdot}CO_2H$	$4{\cdot}7 \times 10^{-2}$ min^{-1}	Fast (10 sec)	See discussion	Complete
C_5H_5N	Fast (5 min)*	Fast (10 sec)	60% complete*	Complete
$SC(NH_2)_2$	Fast (5 sec)	Fast (10 sec)	Complete	Complete
OH^-	Fast (5 sec)	Fast (5 sec)	Complete	Complete

* Equilibrium is established in these cases.

TABLE 4.

(1) *cis*- $Pd(DH_2)_2BNO_2 + B \xrightarrow{k}$ *cis*- $Pd(NH_2)_2B_2 + NO_2$
(2) *trans*- *trans*-

CONCENTRATION OF B AND COMPLEX 0·0005 M. TEMP 36°C

Incoming group B	Rate constants, or maximum time for change		Remarks	
	k_1	k_2	(1)	(2)
H_2O	—	—	No reaction	No reaction
$C_6H_5{\cdot}NH_2$	$6{\cdot}4 \times 10^{-2}$ min^{-1}*	$3{\cdot}8 \times 10^{-2}$ min^{-1}*	Rate zero order in reagent	Rate zero order in reagent
$H_2N{\cdot}CH_2{\cdot}CO_2H$	1·0 (l. mole^{-1} min^{-1})	1·16 (l. mole^{-1} min^{-1})	S_N2 60% complete	S_N2 complete
C_5H_5N	0·28 (l. mole^{-1} min^{-1})	0·5 (l. mole^{-1} min^{-1})	S_N2 60% complete	S_N2 complete
$SC(NH_2)_2$	Fast (5 sec)	1·56 (l. mole^{-1} min^{-1})	Complete	S_N2 complete
OH^-	Fast (5 sec)	Fast (5 sec)	Complete	Complete

* The same rate constants were obtained when the concentration of B in solution was 0·0005 M, 0·0095 M, 0·0195 M and 0·0395 M.

where an equilibrium was established before C_∞ could be reached, the theoretical value of C_∞ was used assuming normal and complete reaction. The results obtained are given above (Tables 1–4).

DISCUSSION

In studying the reactions by the conductance method it has been assumed that normal products are formed, resulting from the successive replacement of the two acid groups by the reagent. This is justified by the fact that a few of the expected

reaction products are already known[13] and that the final value of the conductance in many cases agreed fairly closely to that expected on the basis of the normal course of reaction.

In the case of the reaction between dichloroethylenediaminepalladium(II), which exists as a chloro-aquo complex in aqueous solution (cf. Table 1), and glycine it has been found that on mixing the two reactants there is an immediate and considerable fall in pH and that the final value of the conductance was close to that expected for the following reaction:

$$Pd(en)(H_2O)Cl^+ + H_2N{\cdot}CH_2{\cdot}CO_2H \longrightarrow (en)Pd^{+}\!\!<\!\!\begin{matrix}NH_2\\ O_2C\end{matrix}\!\!>\!CH_2 + H^+ + Cl^- + H_2O$$

Since a perfect second-order plot was obtained the following mechanism is excluded,

$$Pd(en)(H_2O)Cl^+ + H_2N{\cdot}CH_2{\cdot}CO_2H \xrightarrow[-H_2O]{\text{fast}} Pd(en)(H_2N{\cdot}CH_2CO_2H)Cl^+$$

$$\downarrow \text{slow}$$

$$(en)Pd^{+}\!\!<\!\!\begin{matrix}H_2N\\ O_2C\end{matrix}\!\!>\!CH_2 + H^+ + Cl^-;$$

as in this case the rate-determining step would have been a first order reaction. In the reaction of the *cis*-dinitrodiamminepalladium(II) with glycine it has been found that in equimolar solutions of the two reactants there is an instantaneous rise in conductance to a value expected for a uni-univalent electrolyte, followed by a further increase presumably due to the following change:

$$cis\text{-}Pd(NH_3)_2(NO_2)_2 + H_2N{\cdot}CH_2{\cdot}CO_2H \xrightarrow{\text{fast}} cis\text{-}Pd(NH_3)_2(NO_2)(H_2N{\cdot}CH_2CO_2H)^+ + NO_2^-;$$

$$cis\text{-}Pd(NH_3)_2(NO_2)(H_2N{\cdot}CH_2{\cdot}CO_2H)^+ \xrightarrow{\text{slow}} Pd^{+}(NH_3)_2\!\!<\!\!\begin{matrix}NH_2\\ O_2C\end{matrix}\!\!>\!CH_2 + HNO_2;$$

$$HNO_2 \rightleftharpoons H^+ + NO_2^-.$$

Although the final value of the conductance was not equal to that expected on the basis of the above mechanism and the known dissociation constant (ca. 4×10^{-4}) of nitrous acid, a perfect first order plot was however obtained by using the theoretical value and thereby justified the above mechanism. If, however, the complex and glycine are mixed in 1 : 2 molar proportions the following change takes place:

$$cis\text{-}Pd(NH_3)_2(NO_2)(GH)^+ + GH \longrightarrow cis\text{-}Pd(NH_3)_2(GH)_2^{+2} + NO_2^-$$

which obeys the second order rate law. This reaction, being much faster than the

[13] E. FISCHER, *Pogg. Ann.* **71**, 431 (1847); J. A. MÜLLER, *J. prakt. Chem.* **59**, 29 (1853); J. N. FRIEND, *Textbook of Inorganic Chemistry* Vol. 10, p. 208 *et seq.* Charles Griffin, London (1928).

chelation reaction taking place in the equimolar mixture (cf. Tables 3 and 4), dominates over the latter in the 1 : 2 molar solution of the complex and glycine.

From the results summarized above in Tables 1–4 it is quite apparent that the rates of substitution in palladium(II) complexes vary from quite fast to slow, comparable to that already observed in the platinum(II) series.[9] A comparison of the rates of replacement of one Cl by H_2O in the following platinum and palladium compounds, however, shows some significant difference:

trans-	$PdCl_2(NH_3)_2$	$k = 2{\cdot}3 \times 10^{-2}$ min^{-1} at 36°C.
(*cis*)	$PdCl_2$en	Very fast at 36°C.
trans-	$PtCl_2(NH_3)_2$	$k = 0{\cdot}6 \times 10^{-2}$ min^{-1} at 25°C.
(*cis*)	$PtCl_2$en	$k = 0{\cdot}32 \times 10^{-2}$ min^{-1} at 25°C.

While, in the Pt compounds the *trans*-reacts about twice as fast as the *cis*-, in the Pd compounds the *cis*-reacts faster by several powers of ten than the *trans*-, despite the fact that this has a rate constant comparable with that of the *trans*- Pt compound. This difference in behaviour of the *cis*- and *trans*- complexes of platinum(II) and palladium(II) indicates that the *trans*-effect is insignificant in the latter. Hence, owing to its non-symmetry the *cis* complex, dichloroethylenediaminepalladium(II), reacts much more rapidly.

Furthermore, for the same complex the rate is directly dependent on the nucleophilic character of the incoming group. Hence, the hydroxide ion, which is not at all a good reagent for platinum(II) complexes[9] is extremely powerful for palladium(II) complexes, as it is in the cobalt(III) and chromium(III) series.[14] All the reagents that have been studied react by S_N2 processes and this is also possibly true for water, but this cannot be decided positively by kinetic measurements in aqueous solution. The only exceptions are the reactions of aniline with

$$\textit{cis}\text{- and }\textit{trans}\text{-}Pd(NH_3)_2(NO_2)(C_6H_5NH_2)^+$$

where the rate is independent of aniline concentration but is possibly S_N2 in water followed by reaction of the aquo complex with aniline to form the product. The S_N2 rates have been found to decrease more or less in the following sequence of the reagents:

$$OH^- > SC(NH_2)_2 > C_5H_5N > H_2N{\cdot}CH_2{\cdot}CO_2H > C_6H_5{\cdot}NH_2 > H_2O.$$

This is also more or less the decreasing order of nucleophilic character of these groups.[15] The rather strong nucleophilic character of thiourea, which as a base is much weaker than pyridine, is believed[16] to be due to the great polarizability of the sulphur atom. Hence, it is the nucleophilic character and not the π-bonding ability which determines the reactivity of a reagent towards palladium(II) complexes. Thiourea being both π-bonding as well as strongly nucleophilic is a good reagent for both platinum(II) and palladium(II) complexes; but the hydroxide ion is strongly nucleophilic and not at all π-bonding in character and as such it is a powerful reagent for palladium(II) complexes and is extremely weak for platinum(II) complexes. Water being weakly nucleophilic and having no π-bonding character, is not a good reagent for either series. Both palladium(II) and platinum(II) complexes, therefore,

[14] F. Basolo, *Chem. Rev.* **52**, 459 (1955).
[15] C. G. Swain and C. B. Scott, *J. Amer. Chem. Soc.* **75**, 141 (1953); J. O. Edwards, *Ibid.* **76**, 1540 (1954).
[16] R. G. Pearson, S. H. Langer, F. V. Williams and W. J. McGuire, *J. Amer. Chem. Soc.* **74**, 5130 (1952).

show more or less the same degree of lability towards water, showing that the complexes of platinum(II) and palladium(II) do not fundamentally differ much in their lability.

Again, *trans*-dinitrodiamminepalladium(II) reacts with aniline at a measurable rate in contrast to the corresponding dichloro complex. This indicates that the nitro group, which is so powerfully *trans*-activating in platinum(II) complexes, does not have the same π-bonding, *trans*-activating effect in the palladium(II) complexes. The difference in behaviour of the platinum(II) and palladium(II) complexes can be explained as follows:

The five-co-ordinated intermediate formed in the transition state utilizes the vacant 5*p*-orbital in palladium(II) while in platinum(II) it is the 6*p*-orbital which is involved. Hence, the transition state will be more readily formed in the former case than in the latter, as the effective charge on the central metal atom is the same in both the cases. In the case of platinum(II), where from energetic considerations 5*d*- and 6*p*-orbitals can combine to form hybrid *dp*-orbitals suitable for π-bond formation with a ligand,[6,17] the electron affinity of the platinum is so much increased as to favour the formation of the five-co-ordinated intermediate due to π-bonding. Hence, lability to substitution in complexes of platinum(II) depends among other factors largely on the π-bonding ability of the incoming group[9] or of any group already present in the complex;[5-8] while in the palladium(II) series, where π-bonding cannot be significant,[6] lability to substitution depends considerably on the nucleophilic character of the incoming group, as has been observed during the present investigations.

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[17] J. CHATT and L. A. DUNCANSON, *J. Chem. Soc.* 2939 (1953).

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THE NITRATE COMPLEXES OF TETRAVALENT PLUTONIUM

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Abstract—An equilibration technique using liquid amines possessing ion exchange properties has been used to study the nitrate complexes of tetravalent plutonium. It has been shown that practically all the plutonium present in nitrate salt solutions above 1 M or in 1–4 M nitric acid is present as undissociated $Pu(NO_3)_4$. The plutonium species predominating in the amine phase has been shown to be $R_2Pu(NO_3)_6$. A study of the spectra in liquid amine–toluene solution and in 11 M nitric acid has led to the conclusion that $H_2Pu(NO_3)_6$ is the sole tetravalent plutonium species present in strong nitric acid. Spectra at intermediate nitric acid concentrations (4–11 M) suggest the possibility of the existence of $HPu(NO_3)_5$.

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THE recovery of plutonium from irradiated nuclear reactor fuels by aqueous processing methods normally involves dissolution in nitric acid and extraction of the fissionable and fertile materials from either a nitric acid or a nitrate salt medium. This is true of the Purex and Redox processes used in the United States, the Butex process used in Great Britain and the Anion Exchange process used in Canada. Attempts to obtain a quantitative interpretation of the basic chemistry of these processes are frustrated by lack of knowledge of the chemistry of plutonium in nitrate solutions. An attempt has therefore been made to determine the relative concentrations of the various complex ions of plutonium in nitrate solutions.

METHOD

The experimental method employed is similar in principle to that used by CONNICK and MCVEY in their study of the aqueous chemistry of zirconium.[1] By equilibrating various aqueous zirconium solutions with thenoyltrifluoroacetone–benzene solutions they were able to identify certain complex zirconium cations in the aqueous solutions and were able to calculate equilibrium constants for their formation.

Amines possessing ion exchange properties will extract anionic plutonium complexes from nitrate solutions and thus offer a method of determining the complex plutonium ion species present in nitrate solutions. In this work Rohm and Haas Amine 9D-178,[2] a mixture of highly branched, unsaturated, secondary aliphatic amines of molecular weights principally 351–393, diluted with toluene, was used as the extracting agent.

In order to analyse the extraction data obtained, it is first necessary to make an assumption regarding the plutonium species which are present. Here it is assumed that in 0·2 M nitric acid containing various amounts of sodium nitrate and sodium perchlorate, essentially all the plutonium exists in the following forms: Pu^{4+}, $Pu(NO_3)^{3+}$, $Pu(NO_3)_2^{2+}$, $Pu(NO_3)_3^{+}$, $Pu(NO_3)_4$, $Pu(NO_3)_5^{-}$, $Pu(NO_3)_6^{2-}$, $HPu(NO_3)_5$ and $H_2Pu(NO_3)_6$. Two forms were assumed to exist in the organic phase, viz. $RPu(NO_3)_5$ and $R_2Pu(NO_3)_6$, where R refers to the "liquid ion exchange resin" matrix.

(1) R. E. CONNICK and W. H. MCVEY, *J. Amer. Chem. Soc.* 71, 3182 (1949).
(2) Brochure S.P.–69, Rohm and Haas Co., Washington Square, Philadelphia 5, Pa.

For an equilibrium mixture of these eleven species it is possible to write ten independent equilibrium relationships. The choice of these relationships is arbitrary provided that they are independent of one another. The equations which are written below were chosen to yield a tractable final expression.

$$Pu(NO_3)_n^{(4-n)+} + (4-n)NO_3^- + 2HNO_3 \underset{}{\overset{K_n}{\rightleftharpoons}} H_2Pu(NO_3)_6$$

$$n = 0, 1, \ldots, 6$$

$$HPu(NO_3)_5 + HNO_3 \underset{}{\overset{K_7}{\rightleftharpoons}} H_2Pu(NO_3)_6$$

$$H_mPu(NO_3)_{4+m(aq)} + mRNO_{3\,(org)} \underset{}{\overset{K_{m+7}}{\rightleftharpoons}} R_mPu(NO_3)_{4+m(org)} + mHNO_{3(aq)}$$

$$m = 1, 2$$

Writing the expression for the thermodynamic equilibrium constant for each equation and rearranging we obtain

$$Pu^{(4-n)+} = \frac{\gamma_{H_2Pu}}{K_n \gamma_n^{4-n} \gamma_H{}^2 \gamma Pu^{(4-n)+}} \cdot \frac{H_2Pu}{N^{4-n}H^2} \equiv K_n' \frac{H_2Pu}{N^{4-n}H^2} \tag{1}$$

$$n = 0, 1, \ldots, 6$$

$$HPu = \frac{\gamma_{H_2Pu}}{K_7 \gamma_H \gamma_{HPu}} \cdot \frac{H_2Pu}{H} \equiv K_7' \frac{H_2Pu}{H} \tag{2}$$

$$\frac{R_mPu}{H_mPu} = \frac{K_{m+7}\, \gamma_{H\,mPu}\, \gamma_{RN}{}^m}{\gamma_{R_mPu}\, \gamma_H{}^m} \cdot \frac{RN^m}{H^m} \equiv K'_{m+7} \frac{RN^m}{H^m} \tag{3}$$

$$m = 1, 2$$

where Pu^{4+} is the concentration of Pu^{4+} in the aqueous phase
Pu^{3+} is the concentration of $Pu(NO_3)^{3+}$ in the aqueous phase
Pu^{2+} is the concentration of $Pu(NO_3)_2{}^{2+}$ in the aqueous phase
Pu^{+} is the concentration of $Pu(NO_3)_3{}^{+}$ in the aqueous phase
Pu is the concentration of $Pu(NO_3)_4$ in the aqueous phase
Pu^{-} is the concentration of $Pu(NO_3)_5{}^{-}$ in the aqueous phase
Pu^{2-} is the concentration of $Pu(NO_3)_6{}^{2-}$ in the aqueous phase
HPu is the concentration of $HPu(NO_3)_5$ in the aqueous phase
H_2Pu is the concentration of $H_2Pu(NO_3)_6$ in the aqueous phase
N is the concentration of $NO_3{}^-$ in the aqueous phase
H is the concentration of molecular HNO_3 in the aqueous phase
RN is the concentration of RNO_3 in the solvent phase
RPu is the concentration of $RPu(NO_3)_5$ in the solvent phase
R_2Pu is the concentration of $R_2Pu(NO_3)_6$ in the solvent phase
γ's represent the appropriate activity coefficients
K's represent the appropriate thermodynamic equilibrium constants.

Eliminating HPu from (3) and adding the two equations (3), we obtain

$$\frac{RPu + R_2Pu}{H_2Pu} = \frac{K_7'K_8'RN + K_9'RN^2}{H^2} \tag{4}$$

By material balance (T denoting "total"),

$$Pu_T = \sum_{n=0}^{n=6} Pu^{(4-n)+} + \sum_{m=1}^{m=2} H_mPu \tag{5}$$

Combining equations (1) and (2) with equation (5) and rearranging, we have

$$H_2Pu = \frac{Pu_T}{\sum_{n=0}^{n=6} K_n'/N^{4-n}H^2 + K_7'/H + 1} \tag{6}$$

H_2Pu is eliminated from (4) by substitution from (6) and the resulting expression is rearranged to give

$$K_{Pu} = \frac{RPu + R_2Pu}{Pu_T} = \frac{K_7'K_8'RN + K_9'RN^2}{\sum_{n=0}^{n=6} K_n'/N^{4-n} + K_7'H + H^2} \tag{7}$$

where K_{Pu} is the measured plutonium partition coefficient.

If equation (7) is to be useful in a quantitative determination of the plutonium species present in both phases, four major requirements have to be satisfied, viz.:

(1) RN must be determinable. If the plutonium concentration in the solvent phase is kept low with respect to the concentration of the amine, the contribution of RPu and R_2Pu can be neglected without introducing a significant error into the solutions of the equation.

(2) There should be no plutonium species present in appreciable quantity other than the eleven assumed species. If, for instance, hydrolysis products were present in the experimental system a solution of equation (7) could lead to anomalous results, viz., negative equilibrium constants. The experimental work that follows demonstrates quite unambiguously that this assumption is sound.

(3) The constants K_1'–K_9' are not true constants but contain activity coefficients as is shown in equations (1–3). Consequently in a given series of experiments these activity coefficients should not vary. Two measures were adopted to ensure this. Firstly, the concentration of RNO_3 in the solvent phase was kept low ($<10^{-1}$ M) so that γ_{RN}, γ_{RPu} and γ_{R_2Pu} remained constant. Secondly, the ionic strength of the aqueous phase was held constant by adding the appropriate quantity of sodium perchlorate. The effectiveness of this measure is discussed later. Sodium perchlorate was chosen in preference to other salts since perchlorate ion reputedly does not complex plutonium. Extraction of plutonium IV by the amine from perchlorate solution was found experimentally to be insignificant. (For 0·02 N amine and 4 M $HClO_4$, the partition coefficient was $1{\cdot}2 \times 10^{-5}$).

(4) $RPu(NO_3)_5$, $R_2Pu(NO_3)_6$ and RNO_3 must not have any appreciable solubility in the aqueous phase and conversely the remainder of the plutonium species must have negligible solubility in the organic phase.

If these requirements are met, equation (7) can be applied to the extraction data to yield the constants K_0' through K_9'. With a knowledge of these constants the

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concentration of each species in the system can be obtained as a function of nitrate ion and undissociated nitric acid concentrations as shown in the following equations.

$$Pu^{(4-n)+} = \frac{K_n' Pu_T}{N^{4-n}\left(\sum_{n=0}^{n=6} K_n'/N^{4-n} + K_7'H + H^2\right)} \qquad (8)$$

$$n = 0, 1, \ldots, 6$$

$$HPu = \frac{K_7' Pu_T}{\frac{1}{H}\left(\sum_{n=0}^{n=6} K_n'/N^{4-n} + K_7'H + H^2\right)} \qquad (9)$$

$$H_2Pu = \frac{Pu_T}{\frac{1}{H^2}\left(\sum_{n=0}^{n=6} K_n'/N^{4-n} + K_7'H + H^2\right)} \qquad (10)$$

$$RPu = \frac{K_7' K_8' RN\, Pu_T}{\sum_{n=0}^{n=6} K_n'/N^{4-n} + K_7'H + H^2} \qquad (11)$$

$$R_2Pu = \frac{K_9' RN^2\, Pu_T}{\sum_{n=0}^{n=6} K_n'/N^{4-n} + K_7'H + H^2} \qquad (12)$$

It is evident that the validity of the experimental method hinges on the assumption of constant activity coefficients at constant ionic strength. Consequently an experiment was carried out to test this assumption. If we write the thermodynamic equilibrium expression for the reaction

$$ClO_4^- + RNO_3 \underset{}{\overset{K}{\rightleftharpoons}} RClO_4 + NO_3^-$$

remembering that the concentrations of RNO_3 and $RClO_4$ are low, we have

$$K = \frac{(RClO_4)(NO_3)\,\gamma_{NO_3^-}}{(RNO_3)(ClO_4^-)\,\gamma_{ClO_4^-}}$$

and

$$K\frac{\gamma_{ClO_4^-}}{\gamma_{NO_3^-}} = \frac{(RClO_4)(NO_3^-)}{(RNO_3)(ClO_4^-)} \qquad (13)$$

If the right side of equation (13) is constant over a range of nitrate and perchlorate ion concentrations then $\gamma_{ClO_4^-}/\gamma_{NO_3^-}$ must be constant. The variation of this quantity was determined by equilibrating sodium nitrate–sodium perchlorate–0·2 M nitric acid solutions ($\mu = 6{\cdot}7$) with 10^{-2} N amine in toluene and analysing the equilibrated organic phase for perchlorate.[3] The nitrate ion concentration in the organic phase was determined by subtracting the perchlorate ion concentration from the total exchange capacity of the organic phase. A plot of $K\,\gamma_{ClO_4^-}/\gamma_{NO_3^-}$ against aqueous nitrate ion concentration (Fig. 1) shows that $\gamma_{ClO_4^-}/\gamma_{NO_3^-}$ is essentially constant over the range 3–5·5 M nitrate ion. It appears as though the activity coefficient ratio may remain

[3] W. BODENHEIMER and H. WEILER, *Analyt. Chem.* **27**, 12 (1955).

constant well below 3·0 M nitrate ion, but below this value analytical errors become prohibitively large.

Since the experimental evidence pointed to constant activity coefficients in the range 3·0–5·5 M nitrate ion, the plutonium equilibration experiments were carried out in this concentration range. Sodium nitrate–sodium perchlorate–0·2 M nitric acid solutions, in which the sodium nitrate concentration varied from 3·0–5·5 M and the ionic strength was held constant at 6·7, were made about $5{\cdot}4 \times 10^{-3}$ M

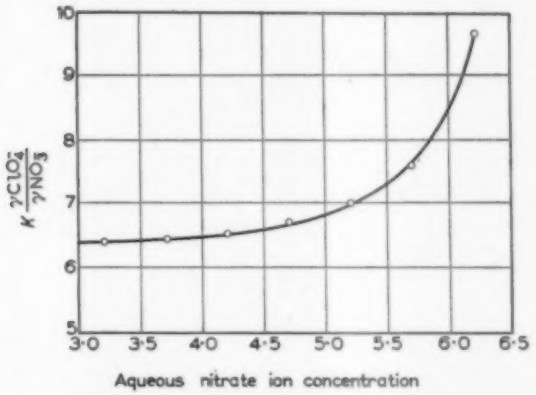

FIG. 1.—Plot of $K\gamma_{ClO_4^-}/\gamma_{NO_3^-}$ vs. aqueous nitrate ion concentration.

in plutonium IV. Aliquots from each solution were equilibrated with a series of amine–toluene solutions varying from 0·002 to 0·04 N amine. At each aqueous nitrate concentration the logarithm of the partition coefficient thus obtained was plotted against the logarithm of the concentration of RNO_3 in the solvent phase. The concentration of RNO_3 in the solvent phase was obtained from a perchlorate analysis of the solvent phase using equation (13) and Fig. 1.

EXPERIMENTAL RESULTS AND DISCUSSION

The plots of log K_{Pu} vs. log RN are shown in Fig. 2. The data give a straight line of slope 1·80. The results of a series of equilibrations in the absence of perchlorate ion, which are pertinent to the interpretation of the data, are plotted in Fig. 3. The slopes at 3·0 and 4·2 M nitrate ion are 2·0 but the slope at 6·5 M nitrate ion drops to 1·86. An examination of equation (7) shows that, according to theory, the curves should be parallel, and if they are straight lines should have a slope of either one or two. The data of Figs. 2 and 3 are interpreted to mean that in the organic phase the plutonium exists essentially entirely in the form $R_2Pu(NO_3)_6$ and that the deviation from the slope of two, where it occurs, is due to the partial failure of one or more of the assumptions underlying the theory.

The significant fact immediately apparent from Fig. 2 is that all the curves in the range 3·0–5·5 M nitrate ion are superimposed. In effect, K_{Pu} does not vary with either nitrate ion or molecular HNO_3 concentration over this region.

Since K_{Pu} is constant over the range 3·0–5·5 M in nitrate ion and approximately 0·03–0·05 M in molecular HNO_3 for a given RNO_3 concentration, the denominator

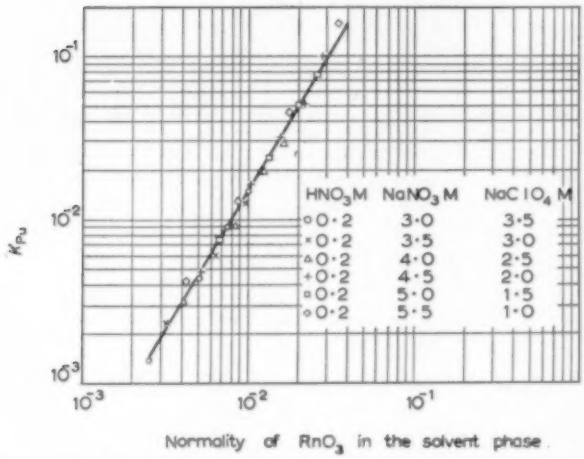

FIG. 2.—Plot of K_{Pu} vs. solvent RNO_3 concentration at constant ionic strength.

of equation (7) is also constant, independent of N and H, in this region. Since the denominator of equation (7) remains constant when both N and H vary, one is forced to the conclusion that the terms containing N or H are negligibly small compared to those not containing N or H. Since the only term in the denominator not containing N or H is K_4' one must conclude that all terms in the denominator are negligibly small in comparison with K_4'. When this result is applied to equations (8–10), one concludes that in this region tetravalent plutonium exists essentially entirely as undissociated $Pu(NO_3)_4$.

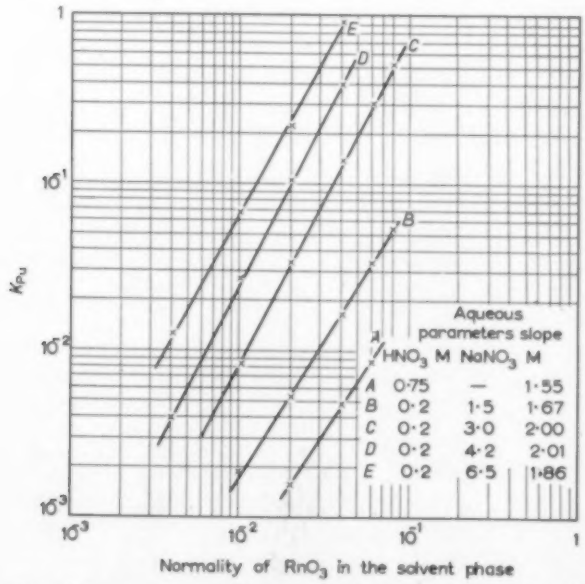

FIG. 3.—Plot of K_{Pu} vs. solvent RNO_3 concentration in the absence of perchlorate ion.

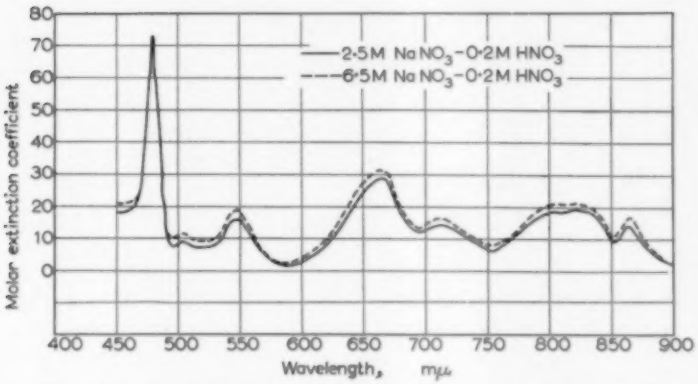

FIG. 4.—Absorption spectra of plutonium IV in sodium nitrate solutions.

A confirmation and extension of this conclusion can be obtained from a combination of spectrophotometric and tributyl phosphate (TBP) equilibrium partition data. The spectra of plutonium IV in 2·5 M sodium nitrate–0·2 M nitric acid and in 6·5 M sodium nitrate–0·2 M nitric acid are identical (Fig. 4) and are also identical with the spectrum of plutonium IV in 2 and 4 M nitric acid (Fig. 5). If these spectra are all identical, it is reasonable to conclude that one species predominates over the whole range and that the other species are present in such small amounts that they do not affect the spectra. If this predominant species is $Pu(NO_3)_4$, as we suggest, then the equilibrium partition coefficient for the reaction $Pu(NO_3)_{4(aqueous)} + 2TBP_{(organic)} \rightleftharpoons Pu(NO_3)_4 \cdot 2TBP_{(organic)}$ will be independent of nitrate ion concentration as long as the equilibrations are carried out at constant ionic strength. However, if the predominant species is $Pu(NO_3)^{3+}$ as suggested by HINDMAN,[4] or any other species than $Pu(NO_3)_4$, then the equilibrium partition coefficient for the above-mentioned reaction must vary with nitrate ion concentration. The results of such an equilibration experiment are given in Table 1. Sodium perchlorate was again used to maintain constant ionic strength since TBP extraction of plutonium IV from perchlorate solutions is insignificant. (For 5% TBP and 1·5 M $HClO_4$–2·5 M $NaClO_4$ the partition coefficient was $6{\cdot}0 \times 10^{-4}$.)

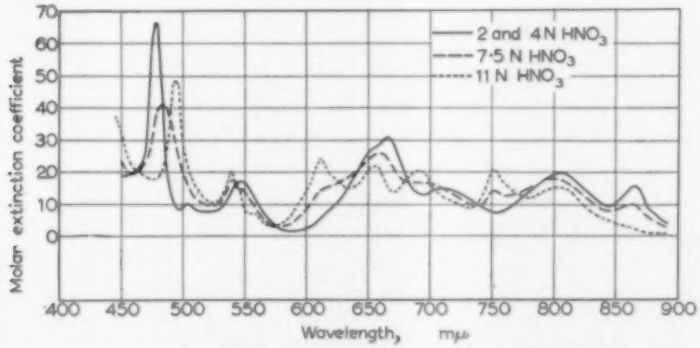

FIG. 5.—Absorption spectra of plutonium IV in nitric acid solutions.

[4] J. C. HINDMAN, *The Transuranium Elements, National Nuclear Energy Series* IV–14B, Paper 4.5. McGraw-Hill, New York (1949).

TABLE 1.—TBP EQUILIBRIUM DATA

$NaNO_3$ (M)	$NaClO_4$ (M)	Ionic strength* (M)	TBP in Soltrol† %	K_{Pu}
4·3	0·2	4·7	5	6·3
3·2	1·3	4·7	5	7·4
2·5	2·0	4·7	5	7·6
0·8	3·7	4·7	5	5·7
4·3	—	4·5	5	5·2
3·2	—	3·4	5	2·2
2·5	—	2·7	5	1·1
0·8	—	1·0	5	0·08

* All samples 0·2 M nitric acid at equilibrium to prevent hydrolysis of Pu^{IV}.
† Soltrol is an inert kerosene-type petroleum fraction.

The data above the broken line in Table 1 show that over the range of nitrate ion concentration studied K_{Pu} is virtually constant at constant ionic strength. The data below the broken line show the wide variation obtained in K_{Pu} at equivalent nitrate ion concentrations when the ionic strength is not held constant. Since K_{Pu} is essentially constant at constant ionic strength from 1·0 M–4·5 M nitrate ion this confirms

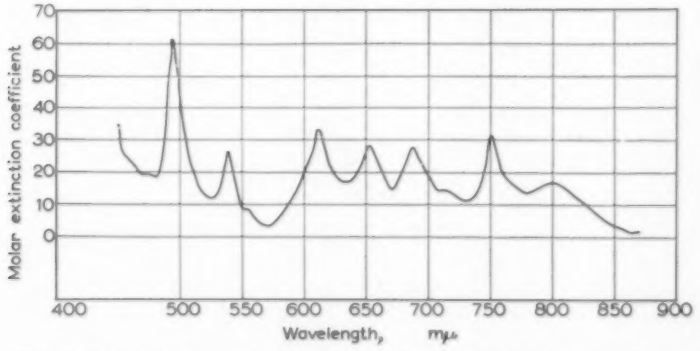

FIG. 6.—Absorption spectra of plutonium IV in amine 9D-178-toluene solution.

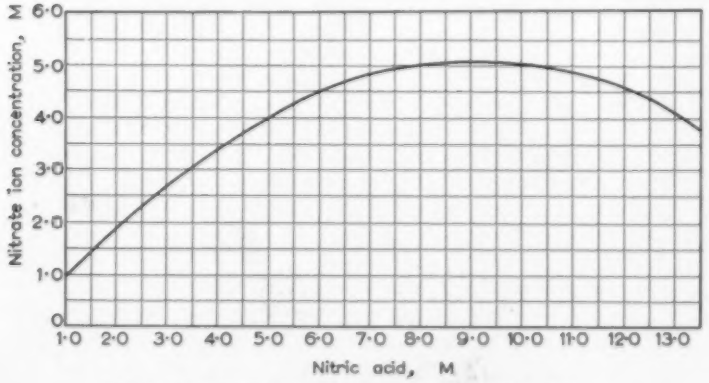

FIG. 7.—Concentration of nitrate ion in nitric acid solutions.

our conclusion that the predominant species is $Pu(NO_3)_4$. When we consider that the partition coefficient is essentially constant down to 1·0 M sodium nitrate and that the spectrum in 2·5 M sodium nitrate is identical with that in 6·5 M sodium nitrate we can extend the range of nitrate salt concentration over which our conclusion holds to 1·0 M at the low end and 6·5 M at the high end.

In nitric acid solution the situation differs considerably. The spectra of plutonium IV at four different acidities are presented in Fig. 5. A comparison between Figs. 4 and 5 indicates that in 2 and 4 M HNO_3 the plutonium is essentially all in the form $Pu(NO_3)_4$ but as the acidity is increased at least one, and possibly two (in the light of the behaviour in the region 470–500 μ) new plutonium species are formed. Since the free nitrate ion concentration in nitric acid goes through a maximum of 5·0 M (Fig. 7)[5] and no change in spectrum is observed in nitrate salt solutions up to a free nitrate ion concentration of 6·5 M, one is forced to the conclusion that the observed change in the spectrum in nitric acid is due to the appearance of a reaction product (or products) between $Pu(NO_3)_4$ and molecular HNO_3. Further, there is no change in the plutonium IV spectrum above 11 M nitric acid. This suggests that at and above 11 M nitric acid a new single species predominates. In our extraction studies it was demonstrated that the plutonium species present in the organic phase was $R_2Pu(NO_3)_6$. The spectrum of this species is presented in Fig. 6. It can be seen to be nearly identical with the plutonium spectrum in 11 M nitric acid The combined evidence suggests quite strongly that at and above 11 M nitric acid plutonium IV exists almost entirely as undissociated $H_2Pu(NO_3)_6$. The behaviour of the spectrum in the region 470–500 μ may possibly suggest that at acidities intermediate between 4 M and 11 M the species $HPu(NO_3)_5$ exists in appreciable quantity.

[5] H. A. C. McKay, *Trans. Faraday Soc.* **52**, 1568 (1956).

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J. Inorg. Nucl. Chem., 1958, Vol. 7, pp. 94 to 112. Pergamon Press Ltd., London

PROTACTINIUM—III

SOLVENT EXTRACTION FROM HALIDE SOLUTIONS*

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Abstract—The extraction of protactinium from chloride solutions by a number of organic solvents has been investigated and the effects of the acidity and chloride concentrations in the aqueous phase measured. It is shown that these and other results can be explained in terms of the distribution between the two phases of an ion-pair complex formed by a chloro-anion containing the metal and an "onium" cation containing water and solvent molecules. The extracting power of the solvent therefore depends on its base strength, or ability to form the cationic complex, as well as its dielectric constant. Dissociation or association of the ion-pairs may become important in the organic phase, so that departures from a simple distribution law may be found at some concentrations of the extracting metal. These departures can be correlated with the dielectric constant of the solvent. The effect on the extraction of strong acids, such as perchloric acid, and the use of solutions of the higher amines in benzene and benzonitrile are explained in terms of this model. Extraction from sulphate and thiocyanate solutions has also been investigated.

DURING the last ten years considerable progress has been made toward the elucidation of the processes whereby metals can be extracted from aqueous solutions of their salts by organic solvents. A substantial proportion of these investigations has related to solutions of the metal halides and, as a result, a model for the extraction process, which will account for most of the experimental data, has emerged. The extraction of trivalent gold and iron from solutions of their chlorides in hydrochloric acid has received the most detailed consideration, but some important features of the model have been established in studies of the halides of the elements in the third main group of the Periodic classification.

In the previous papers in this series procedures for the solvent extraction of protactinium from nitrate[1] and halide[1,2] solutions have been described. Further investigation of the conditions for this extraction, together with a study of the comparative merits of different solvents, has provided data that can be examined in relation to this model.

In some systems, particularly when iodides are involved, the principal species extracted are the neutral metal halides. The extraction of stannic iodide by carbon tetrachloride[3,4] is a clearly established example; and the mercury halides may extract in the same way.[5,6] But for a number of metals it has been shown that the

* Paper II in this series, *The Solvent Extraction of Protactinium*, appeared in the *Canad. J. Chem.* **34**, 284 (1956).

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[4] J. H. HILDEBRAND and G. J. ROTARIU, *Analyt. Chem.* **24**, 771 (1952).
[5] A. HANTZSCH, *Z. phys. Chem.* **30**, 258 (1899).
[6] F. MYLIUS and G. HÜTTNER, *Ber. dtsch. chem. Ges* **44**, 1315 (1911).

solvent extracts from acid solutions a complex halo-acid. The evidence for the identity of these species has been discussed in detail by IRVING and his collaborators [7–13] in a recent series of papers. Analytical data for iron,[14–17] gallium,[18,19] gold[6] and indium[9] showed that the complex passing into the organic solvent contains the metal, acidic hydrogen and the halogen in the atomic ratios 1 : 1 : 4. In the case of iron, it has been shown that the absorption spectrum of the solute in the organic extract is essentially the same as that of solid potassium chloroferrate.[20,21] The same spectrum also appears in a very acid, but not too concentrated, aqueous solution of ferric chloride. The existence of the $InBr_4^-$ unit in the ethereal extract from an acidic solution of indium bromide has been demonstrated by detection of its characteristic Raman spectrum.[22]

All these complex acids, of general formula HMX_4, must be strong acids since no covalent forms of such molecules are likely. They must exist in the organic phase, therefore, as ions, ion-pairs or more complex ionic aggregates. It is inevitable that the hydrogen ions will be solvated. The amount of water accompanying chloroferric acid into the solvent has been measured carefully. These measurements have shown that, if the concentration of iron is not too high, about five molecules of water are transferred to the solvent layer with each molecule of chloroferric acid.[23] More recently an anhydrous suspension of the di-etherate of chloroferric acid in di-*iso*propyl ether, prepared by passing gaseous hydrogen chloride into a solution of anhydrous ferric chloride in di-*iso*propyl ether, has been shown to react with five molecules of water to give a solution, possible containing $H_3O^+ \cdot 4H_2O \cdot FeCl_4^-$ pairs, which is identical in properties with the usual ethereal extract.[24] The anhydrous solution presumably contained diethyl oxonium chloroferrate which has been described previously.[25] The absorption spectra of the anhydrous and the aquated ethereal solutions were identical, although quite different from that of the anhydrous solution of ferric chloride in the ether.

The model outlined above does not ascribe any specific role to the solvent. However, by diluting the solvent with a second entirely inert solvent, which is incapable of extracting the metal by itself, it has been shown that the extracted complex involves molecules of the first solvent.[26–28] The number of molecules of

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[23] R. J. MYERS, D. E. METZLER and E. H. SWIFT, *J. Amer. Chem. Soc.* **72**, 3767 (1950).
[24] A. H. LAURENNE, D. E. CAMPBELL, S. E. WIBERLEY and H. M. CLARK, *J. Phys. Chem.* **60**, 901 (1956).
[25] J. HOUBEN and W. FISCHER, *J. prakt. Chem.* **123**, 89 (1929).
[26] T. V. HEALY and H. A. C. MCKAY, *Rec. trav. Chim.* **75**, 730 (1955).
[27] D. F. PEPPARD, J. P. FARIS, P. R. GRAY and G. W. MASON, *J. Phys. Chem.* **57**, 295 (1953).
[28] H. IRVING and F. J. C. ROSOTTI, *J. Chem. Soc.* 2475 (1956).

the solvent in the extracted complex can be deduced from the slope of a plot of the logarithm of the extraction coefficient versus the mole fraction, at low concentrations of the complexing solvent, for a series of experiments using an aqueous phase of constant initial composition. This procedure has been used to demonstrate the part played by the solvent in the extraction of the indium and protactinium halides.[1,2,28]

Another source of evidence for complexing by the solvent is found in a comparison of the behaviour of different solvents. The extraction coefficients for the metal, from an aqueous phase of constant initial composition, displayed by different solvents can be correlated with their base strengths, or the donor powers of the solvents with respect to hydrogen ions.[29–31] Indeed, the same correlation appears to be found for both the extraction of nitrates and halides. Such a relation should define an order for a series of solvents which should be the same for a wide variety of metals. Existing evidence provides some support for such a series, although some anomalies have been noted.[9,13] However, it is doubtful if the determinations of the extraction coefficients have always been made under comparable conditions.

No detailed description of how the solvent molecules are associated with the extracting complex has yet appeared, although it has been suggested that oxonium ion formation may be involved.[16,52]

Difficulties that were experienced in obtaining a sufficient supply of di-*iso*propyl ketone, a solvent that has been found very suitable for the extraction of the protactinium halides, have led to a comparison of a variety of other solvents. This study has in turn led to some consideration of the factors determining the behaviour of the individual solvents and the identity of the extracting complexes.

EXPERIMENTAL

1. *Materials*

(a) *Solvents*. All solvents, whether of analytical or technical quality, were carefully purified by fractional distillation, through a 2 ft fractionating column, shortly before use. In each case, the fraction used boiled over a range of not more than 1° about the published boiling points. The presence of a contaminant in a solvent often modifies its extraction properties considerably and for some solvents special care was necessary. For instance, the presence of peroxides considerably reduces the extraction of protactinium from chloride solutions by ethers; thus the extraction coefficient, determined with a given aqueous phase, decreases with the period of storage of initially pure dichlorodiethyl ether. The influence of hydrogen peroxide on the extraction of protactinium has been observed by MOORE.[32] Indeed, the reagent is convenient for the re-extraction of protactinium from the organic into an aqueous phase.[33] The ethers were treated, therefore, to remove the peroxides, by shaking with acidified ferrous sulphate before the distillation.

In other cases the contaminant may lead to greatly increased extraction. A technical sample of tributyl phosphate, probably containing small amounts of the acidic mono- and dibutyl phosphates, was found to behave quite differently from the pure material (*vide infra*). A specially purified sample of the solvent was kindly supplied by the Chemistry Division at A.E.R.E., Harwell. Finally, it has been observed that mixtures of solvents sometimes develop quite different extraction properties from those of the separate solvents. This behaviour will be reported in detail in a subsequent publication. Since it was first observed in a mixture of a carbinol and a ketone, and each of these not infrequently occurs as an impurity in the other, particular care was taken by repeated fractionation to ensure that these solvents were pure.

[29] V. LENHER, *J. Amer. Chem. Soc.* **35**, 546 (1913).
[30] V. I. KUZNETSOV, *J. Gen. Chem.* (*U.S.S.R.*) **17**, 175 (1947).
[31] A. W. WYLIE, *J. Chem. Soc.* 1474 (1951).
[32] F. L. MOORE, *Analyt. Chem.* **28**, 997 (1956).
[33] R. ELSON, G. W. MASON, D. F. PEPPARD, P. A. SELLARS and M. H. STUDIER, *J. Amer. Chem. Soc.* **73**, 4974 (1951).

(b) *Protactinium.* ^{231}Pa. Some hundred milligrams were available from some residues from the AEA uranium refinery at Springfields, Lancs. The extraction process used will be described in another paper appearing shortly.[24] The final purification was conducted by means of three solvent extraction cycles using di-*iso*butyl ketone and chloride solutions. The protactinium was extracted by the ketone from a 8 N hydrochloric acid solution of the protactinium. The extract was washed once with 8 N hydrochloric acid and then re-extracted into the aqueous phase with 2 N hydrochloric acid. The strength of this solution was then increased to 8 N and the extraction cycle repeated. A spectroscopic analysis* of the product from a parallel purification showed that the total impurities constituted less than 2 per cent by weight. The principal impurities detected were traces of iron, aluminium, titanium and silicon.

^{233}Pa. This shorter-lived isotope of protactinium was separated from neutron irradiated thorium nitrate. A few days irradiation at a flux of 10^{11} neutrons/cm^2/sec gave sufficient material for several months use. About a week after the end of the irradiation the salt was dissolved in 8 N hydrochloric acid and the solution allowed to stand 24 hr. The solution was then extracted with di-*iso*butyl ketone. The extract was washed with 8 N hydrochloric acid and then re-extracted into 2 N hydrochloric acid. The cycle was repeated once and the final aqueous phase made 6 N in hydrochloric acid before storage and use.

(c) *Other reagents.* The other reagents were of commercial analytical reagent quality.

2. *Technique*

All operations were carried out using polythene equipment. Aqueous solutions and reagents were stored in polythene vessels.

In all the extraction experiments, 1 ml each of the solvent and aqueous phases were equilibrated. The aqueous phase was prepared by the addition of an appropriate aliquot of the protactinium stock to a much larger volume of solution containing the desired concentrations of acid and, in some cases, salts. The volumes used were such that the addition of the protactinium solution had no appreciable effect on the concentrations of chloride and free acid in the aqueous solution. This was occasionally verified by volumetric analysis of the final solution. With the exception of the experiments involving tributylamine, all the solvents were pre-equilibrated with the appropriate inactive acidic aqueous phase before use. Equilibration was achieved by agitation of the mixtures in snap-closure polythene capsules in a mechanical shaker for 10 min. Room temperature varied between 20° and 22°. Previous work has shown that these extractions are not very sensitive to changes of temperature so that thermostating the capsules did not seem necessary.[1] Longer periods of equilibration were found unnecessary in the systems described in this paper. Separation of the phases after equilibration was enhanced when necessary by centrifugation.

In the ion-exchange experiments a similar procedure was used. 100 mg of the ion-exchange resin, previously equilibrated with hydrochloric acid of the requisite strength, was mixed with 0·5 ml of the protactinium solution in a polythene capsule and the capsule agitated for 3 days.

The paper chromatographic experiments were conducted by the ascending front technique using 20 cm strips of 1 cm wide Whatman No. 1 paper. The solvent was pre-equilibrated with 3 N hydrochloric acid before use and the chromatogram chamber was saturated with the vapour from this acid. After development, the R_f value was determined by scanning the strip with a Geiger counter, fitted with a narrow slotted window.

3. *Measurements*

^{233}Pa was measured by evaporating a suitable aliquot of the solution onto a copper foil, igniting at 200°C, and counting under a thin end-windowed Geiger counter in a standard geometrical arrangement. ^{231}Pa was measured on a similarly prepared foil counted under a 2π α-scintillation counter of 35 per cent efficiency. Resin samples were gently ignited until the resin was completely oxidized. In both cases the aliquots chosen were such that the deposits on the foils were effectively infinitely thin for the radiations concerned. No corrections for self-absorption losses were therefore necessary. The extraction coefficient of the protactinium was defined as the ratio of the concentrations of protactinium measured as activity per unit volumes, in the organic and the aqueous phases.

* The authors are indebted to Dr. Birks, A.E.R.E., Harwell for the spectroscopic analyses.

[24] A. G. Goble, J. Golden, A. G. Maddock and D. Toms, To be published.

RESULTS

I. *Factors Influencing the Reproducibility of Results*

In Fig. 1 the results obtained for a pure sample of tributyl phosphate are compared with those obtained for a sample of the commercial product. The profound effect of the traces of the acid phosphates in the latter material is clearly demonstrated. The same effect has previously been reported by FUDGE and WOODHEAD.[35]

Some new evidence of the instability of aqueous solutions of protactinium in

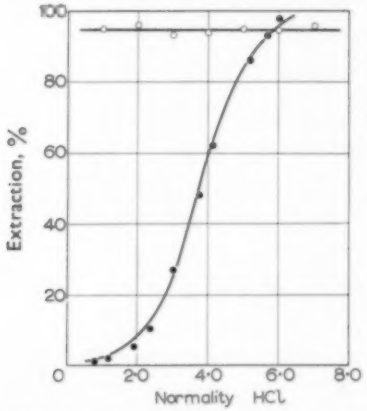

FIG. 1.—Comparison of the behaviour of pure and commercial tributyl phosphate. Experiments conducted with an initial ^{233}Pa concentration in the aqueous phase of 4 to 6 $\times$ 10^{-10} M.
○ Commercial tributyl phosphate
● Pure tributyl phosphate

hydrochloric acid has been obtained. It has been found that even in 6 N hydrochloric acid solutions stored in polythene vessels, protactinium is liable to change from an extractable to an inextractable form. The former appears to consist of one or more relatively simple anionic complexes; the latter, apparently of much higher molecular weight, also possibly comprises several species. At room temperature and under the conditions of storage described above, 6 N hydrochloric acid solutions may be preserved with their extraction properties unchanged for several weeks, but once the transformation has started it proceeds quite rapidly and is usually complete in one or two days. Fig. 2 shows the extraction of protactinium by di-*iso*propyl ketone from a solution in which this process has just begun.

The possibility that oxidation might alter the extraction of protactinium was discounted in the following experiment. Three 1 ml samples of an 8 N hydrochloric acid solution of ^{233}Pa were taken. Two were treated with 100 mg of manganese dioxide; one of them was heated to 50° for 10 min, the other was shaken in the cold for 12 hr. The third acted as a control. Each was then extracted with an equal volume of di-*iso*butyl ketone. No appreciable difference was found between the percentage extraction in the three cases; the values found were 96·2, 96·0 and 96·4 per cent respectively.

Table 1 records data for a similar series of extraction experiments using a stock solution of ^{231}Pa in 6 N hydrochloric acid in which the alteration in properties had

[35] A. J. FUDGE and J. L. WOODHEAD, *Analyst* **81**, 417 (1956).

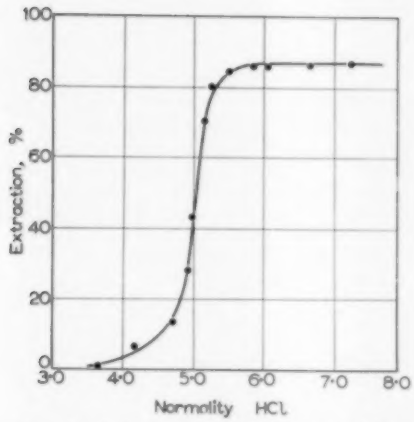

FIG. 2.—Extraction of aged solution of ^{231}Pa by di-*iso*propyl ketone. Aqueous solutions 10^{-5} M in protactinium.

just begun. The values in the fourth column have been calculated on the assumption that the aged solution contained 9·2 per cent of the inextractable form. It can be seen that these data can be interpreted by supposing that all the protactinium is present either as the normal extractable complex or complexes, or in a completely inextractable form. All extraction experiments were therefore conducted with freshly purified material and frequent checks on the extraction properties of the stock solutions were made using solvents of known characteristics. This procedure also avoided difficulties arising from the growth of the decay products in the ^{231}Pa.

TABLE 1.—EXTRACTION OF ^{231}Pa BY DI-*iso*BUTYL KETONE FROM AN AQUEOUS SOLUTION 10^{-5} M IN PROTACTINIUM AT VARIOUS EQUILIBRIUM CONCENTRATIONS OF HYDROCHLORIC ACID

Normality HCl	Extraction fresh ^{231}Pa (%)	Extraction aged ^{231}Pa (%)	Corrected value aged ^{231}Pa (%)
3·06	2·1	—	—
3·58	9·9	—	—
4·04	30·7	26·4	29·1
4·60	67·1	60·0	66·1
5·14	89·5	81·4	89·7
5·50	95·6	87·6	96·5
6·05	—	88·0	—

II. *Extraction of Protactinium from Hydrochloric Acid Solution by Different Organic Solvents*

(a) *Various solvents*

The variation of the percentage of protactinium extracted from an aqueous solution by an equal volume of the solvent was determined as a function of the concentration of hydrochloric acid in the equilibrated aqueous phase for a number of solvents. Fig. 3 shows some results obtained using ^{233}Pa, the initial concentration of protactinium in the aqueous phase being between 4 and 6×10^{-10} M.

The much-used solvent, tributylphosphate can be seen to give a curve that rises more gently than the other solvents. Since the slope of this curve generally determines the specificity of the solvent for the separation of the element, it may be concluded that tributyl phosphate is not a very selective solvent for extraction from chloride solutions.

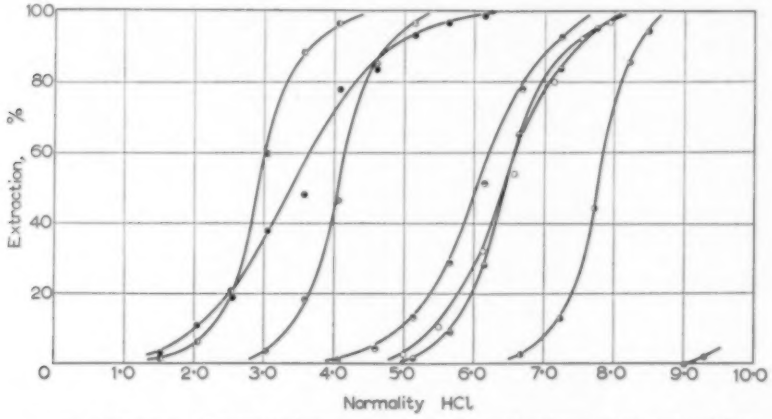

FIG. 3.—Percentage of protactinium extracted by an equal volume of the solvent from an aqueous hydrochloric acid solution as a function of the acidity of the aqueous phase.
Initial concentration of ^{233}Pa in the aqueous phase 4 to 6×10^{-10} M

◐ di-*iso*propyl carbinol
⊖ acetophenone
◒ benzonitrile
⊗ chlorobenzene
● Tributyl phosphate
○ $\beta\beta$-dichlorodiethyl ether
◑ nitrobenzene
◓ 5% tributylamine in benzene (not pre-equilibrated)

(b) *A group of ketones*

Effects of $a_{\pm}$ HCl, $[H^+]$ *and* $[Cl^-]$. Within a given class of compound wide variations in extraction efficiency can occur. The ketones were chosen for the study of these differences. Fig. 4 shows the variation in the extraction coefficient with the activity of hydrochloric acid in the aqueous phase for a number of ketones, the initial aqueous phase containing always between 4 and 6×10^{-10} M of ^{233}Pa. The mean activities of the hydrochloric acid in the solutions used were taken from the data of ÅKERLÖF and TEARE.[36,37] With the exception of *cyclo*hexanone, the plots of the logarithm of the extraction coefficient against the logarithm of the mean activity, $a_{\pm}$, of the acid are a series of nearly parallel straight lines. The exceptional behaviour of the *cyclo*hexanone is undoubtedly due to the considerable mutual solubility of the solvent and the acid at the higher concentrations. Indeed, this curve terminates in a region of complete mutual solubility. At low acidities, the slope of the curve is nearly the same as that of the lines found for the other ketones. Even at fairly low acidities, the pre-equilibration technique used was unable to compensate for the considerable mutual solubility and extraction of acid by this ketone.

The relation between the extraction coefficient and the hydrogen ion concentration, at constant chloride ion concentration of 5 M, was determined for the same solvents. The results are shown in Fig. 5. Again, the plot of the logarithm of the

[36] G. ÅKERLÖF and J. W. TEARE, *J. Amer. Chem. Soc.* **59**, 1855 (1937).
[37] G. ÅKERLÖF and J. W. TEARE, *J. Amer. Chem. Soc.* **60**, 1226 (1938).

extraction coefficient against the logarithm of the hydrogen ion concentration was very nearly linear. It was not possible to explore the effect of the chloride concentration on the extraction coefficients at constant hydrogen ion and total salt concentrations because no other anion without effect on the extraction is known. However, measurements were made on a series of solutions that were all 3 N in

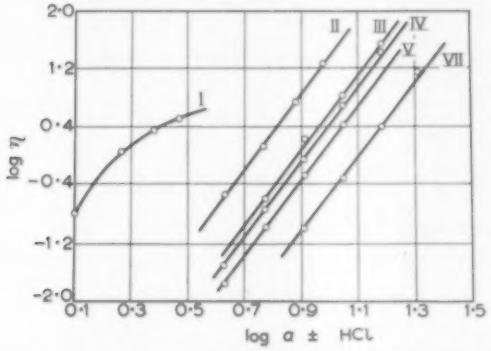

FIG. 4.—Relation between the extraction coefficient, η, and the activity, $a_{\pm}$, of hydrochloric acid in the aqueous phase for a number of ketones. Aqueous phases were initially between 4 and 6×10^{-10} M in ^{233}Pa.

Solvents:
I *cyclo*hexanone, II mesityl oxide, III diethyl ketone, IV acetophenone, V methyl *n*-hexyl ketone, VII di-*iso*butyl ketone.

hydrochloric acid but contained various concentrations of sodium chloride. The data obtained are presented in the usual form in Fig. 6, in which the abscissae denote the logarithm of the total chloride concentration in the aqueous phase.

Ionic character of protactinium in these solutions. In order to gather more information about the state of the protactinium in the aqueous phase in these experiments the behaviour of the aqueous solutions of protactinium in hydrochloric acid on ion exchange resins was re-examined. Values of the distribution coefficient, K_d = activity of protactinium per gramme of resin/activity of protactinium per ml of aqueous phase, were determined for Dowex 1. The samples of resin were pre-equilibrated with hydrochloric acid of the appropriate strength and then treated with a similar strength of acid that was also between 4 and 6×10^{-5} M in ^{231}Pa. The results are displayed in Fig. 7, in which are included some previous results for Dowex 1 obtained by KRAUS and MOORE[38] as well as figures for Dowex 2 and Amberlite IRA 400, previously reported by MADDOCK and PUGH.[39]

Attempted extraction from fluoride solutions. The suppression of the extraction of protactinium by hydrofluoric acid has been known for some time and has been exploited in the separation of the element.[1,32] However, under appropriate conditions a number of other elements can be extracted by solvents from fluoride solutions, including especially tantalum.[40,41,42] No experiments, under conditions likely to encourage extraction, have previously been described for protactinium. Some tests have now been made with methyl *iso*butyl ketone. It has been shown

[38] K. A. KRAUS and G. E. MOORE, *J. Amer. Soc.* **72,** 4293 (1950).
[39] A. G. MADDOCK and W. PUGH, *J. Inorg. Nucl. Chem.* **2,** 114 (1956).
[40] R. BOCK and M. HERRMANN, *Z. anorg. Chem.* **284,** 288 (1956).
[41] F. H. BURSTALL, P. SWAIN, A. F. WILLIAMS and G. A. WOOD, *J. Chem. Soc.* 1497 (1952).
[42] J. WERNING and K. B. HIGBIE, *Industr. Engng. Chem.* **46,** 644 (1954).

that the extraction coefficient for protactinium is less than 10^{-3} for 5, 10 and 15 N hydrofluoric acid solutions.

Influence of sulphuric acid on the extraction. The influence of a strong acid on the extraction of tracer concentrations of protactinium is shown in Table 2, in which

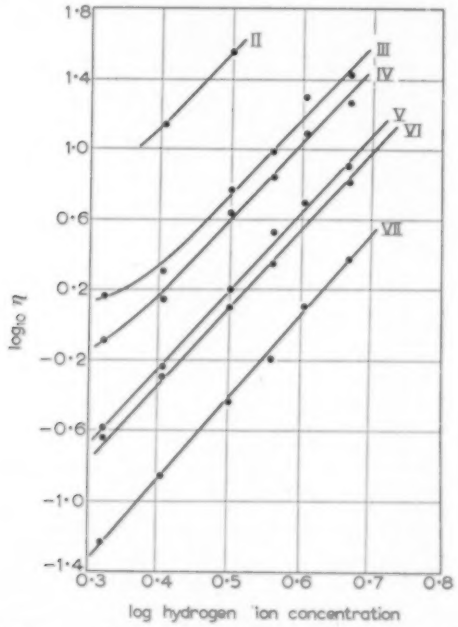

FIG. 5.—Relation between the extraction coefficient, η, and the concentration of hydrogen ions in the aqueous phase at a constant chloride concentration of 5 M, the solutions consisting of mixtures of sodium chloride and hydrochloric acid. Aqueous phases were initially between 4 and 6×10^{-10} M in ^{233}Pa. Solvents: as in Fig. 4 and VI methyl *iso*butyl ketone.

TABLE 2.—^{233}Pa EXTRACTED BY DI-*iso*BUTYL KETONE (PER CENT)

HCl / H_2SO_4	0	2 N	4 N	6 N	8 N
0	1	1	1·5	88	99
2 N	1	1	1	1	3
4 N	2	1	1	1	16
6 N	3	2	2	2	25
8 N	6	3	3	3	72

can be found the approximate percentage extractions of ^{233}Pa by di-*iso*butyl ketone from a variety of mixtures of hydrochloric and sulphuric acids. From pure sulphuric acid solutions some extraction appears to take place. Using the same solvent the following results were obtained:

Normality of acid	2	4	6	8	10	12
Extraction (%)	1·3	2·3	2·8	5·7	7·6	9·0

Both these series of experiments were conducted with solutions of ^{233}Pa of about 10^{-12} M.

(c) *Extraction by some nitro-compounds*

The extractive properties of a number of other solvents were investigated. To facilitate quantitative comparisons between these solvents, the extraction coefficient from an 8 N hydrochloric acid solution of protactinium and the acid concentration

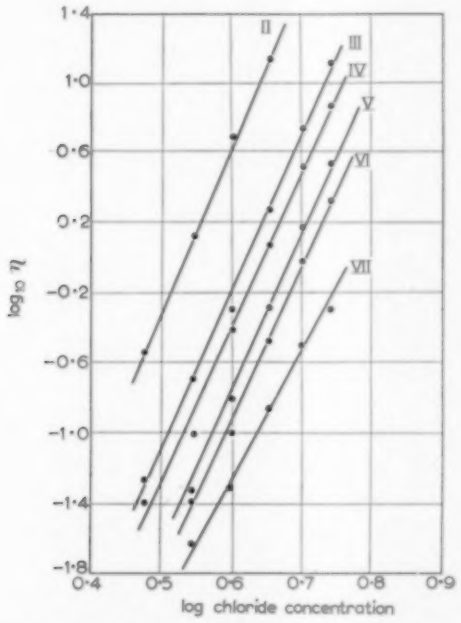

FIG. 6.—Relation between the extraction coefficient, η, and the concentration of chloride at constant hydrogen ion concentration but varying salt concentrations. All aqueous phases 3 N in hydrochloric acid; various concentrations of sodium chloride. Aqueous phases were initially between 4 and 6 $\times$ 10^{-10} M in ^{233}Pa. Solvents: II–VII—see Figs. 4 and 5.

at which the extraction coefficient was one, were determined. Many of the results will be recorded in the figures associated with the discussion (*vide infra*). Nitro benzene, *o*-nitrotoluene and *o*-nitroanisole were studied in rather more detail and the dependence of the extraction coefficient on the mean activity of the hydrochloric acid in the aqueous phase was determined in the same way as for the ketones, using aqueous solutions that were initially between 4 and 6 $\times$ 10^{-10} M in ^{233}Pa. The results are presented in Fig. 8. Parallel measurements were made on nitrobenzene using aqueous solutions that were initially 10^{-5} M in 231 Pa. These results are also included in Fig. 8. The logarithmic plot is a line parallel, but substantially below that obtained from the ^{233}Pa. The ratio of the $^{233}Pa/^{231}Pa$ extraction coefficients at the same acidity is 30. A similar experiment with di-*iso*propyl ketone gave a ratio only slightly greater than 1, while $\beta\beta$-dichlorodiethyl ether gave a ratio of 10; both measurements were made only in 6 M hydrochloric acid solutions.

(d) *Extraction by solutions of amines*

Earlier workers have shown that even the mineral acids can be extracted from aqueous solutions by solutions of the higher tertiary amines.[43] Reference has been made to the extraction of protactinium from chloride solutions by solutions of methyl di-octylamines in chloroform.[44] The variation of the extraction of protactinium by the analogous solution of tributylamine in benzene with the activity

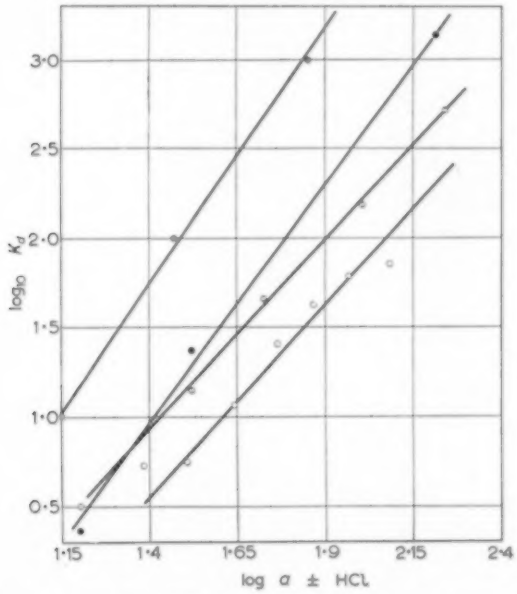

FIG. 7.—Relation between the distribution coefficient, K_d, and the mean activity, $a_{\pm}$, of the hydrochloric acid in the aqueous phase.

○ Dowex 1 (^{231}Pa)
⊗ Dowex 1 (data of KRAUS and MOORE)
● Dowex 2 (Data of MADDOCK and PUGH)
ⓘ Amberlite IRA 400 (Data of MADDOCK and PUGH)
} —^{233}Pa

of the hydrochloric acid in the aqueous phase resembles that found for the other solvents. The results obtained using ^{233}Pa solutions are shown in Fig. 9. Pre-equilibration of the solvent mixture with the inactive aqueous phase was omitted in these experiments to avoid variation in the final tributylamine concentrations. An attempt to extract protactinium from hydrochloric acid solutions by benzene solutions of some of the simpler amines failed owing to extensive precipitation of the amine hydrochlorides.

The role of the bulk solvent in these systems has been explored by comparing the extraction of protactinium from an aqueous phase of constant initial composition by a 5 per cent (weight) solution of tributylamine in a variety of solvents. In Fig. 10 the extraction coefficient for the ^{233}Pa is recorded as a function of the dielectric constant of the pure diluent.

[43] E. LESTER SMITH and J. E. PAGE, *J. Soc. Chem. Industr.* **67**, 48 (1948).
[44] G. W. LEDDICOTTE and F. L. MOORE, *J. Amer. Chem. Soc.* **74**, 1618 (1952).

(e) *Extraction of hydrochloric acid by tributylphosphate*

During pre-equilibration with the inactive aqueous acids in the tributyl phosphate experiments, it was observed that the extraction of hydrogen chloride by this solvent was much more pronounced than for most of the other solvents subjected to a detailed study. A rough distribution curve for the acid was determined by direct

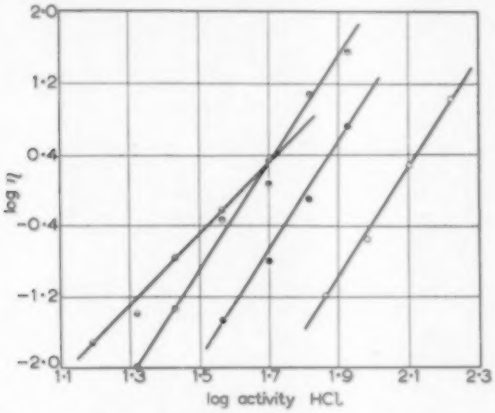

FIG. 8.—Relation between the extraction coefficient, η, and the mean activity, $a\pm$, of the hydrochloric acid in the aqueous phase.

○ *o*-nitroanisole
◒ *o*-nitrotoluene
● nitrobenzene
} all for 4—6 × 10^{-10} M ^{233}Pa
○ nitrobenzene 10^{-5} M ^{231}Pa

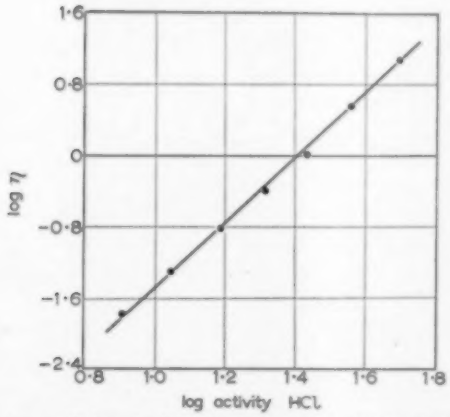

FIG. 9.—Extraction coefficient for ^{233}Pa by 5 per cent (weight) tributylamine in benzene as a function of the activity of the hydrochloric acid, $a\pm$, in the initial aqueous phases, all of which were between 4 and 6 × 10^{-10} M in ^{233}Pa. No pre-equilibration with acid.

titration of aliquots from the two phases after equilibration. The results are shown in Fig. 11.

III. *Extraction of Protactinium from Thiocyanate Solutions*

A brief survey of the extraction of protactinium from thiocyanate solutions by di-*iso*propyl ketone and by amyl acetate was made. The aqueous phase was always

1 N in hydrochloric acid in addition to the thiocyanate content. ^{233}Pa and ^{231}Pa gave very similar results.

Concentration of ammonium thiocyanate, (M)	0	1	2	3
Di-*iso*propyl ketone, extraction (%)	—	0·95	3·4	7·0
Amyl acetate, extraction (%)	—	8·2	10·1	15·9

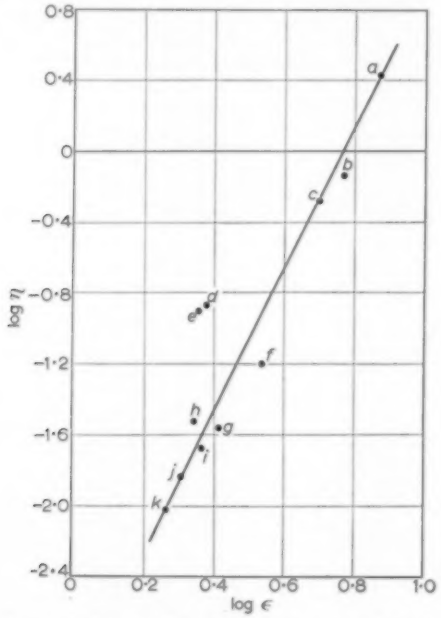

FIG. 10.—Extraction coefficient for ^{233}Pa by 5 per cent (weight) solutions of tributyl amine in various solvents, for an aqueous phase initially 5 N in hydrochloric acid, as a function of the dielectric constant of the pure bulk solvent.
a. *o*-dichlorobenzene, *b*. chlorobenzene, *c*. chloroform, *d*. toluene, *e*. benzene, *f*. trichlorethylene, *g*. carbon disulphide, *h*. carbon tetrachloride, *i*. mesitylene, *j*. *cyclo*hexane, *k*. *n*-heptane.

IV. *Paper Chromatography of Protactinium*

A few experiments were made comparing solvents by a paper chromatographic technique. The experiments were carried out using ^{233}Pa. The chromatograms were developed for 12 hr. The order of R_f values corresponded with that of the extraction efficiencies deduced from the static distribution studies. Cyclohexanone, di-*iso*propyl ketone, acetophenone, methyl *iso*butyl ketone and $\beta\beta$-dichlorodiethyl ether were all used successfully and the order given represents the order of decreasing R_f values and extraction efficiency.

DISCUSSION

Attention must first be drawn to the correction of the data contained in an earlier publication in the series. In this paper higher extraction coefficients were reported for ^{231}Pa (at 0·02 mg/ml) than for ^{233}Pa (at about 10^{-11} M) (Graph 1, ref. (2)). As shown in this paper, the trace concentrations of protactinium actually show a higher extraction coefficient than the macroscopic concentrations at the same concentration of hydrochloric acid. The reason for the earlier erroneous

result has been identified. The sample of ketone used for the ^{231}Pa extraction contained some carbinol and the mixture extracts protactinium more readily than the pure ketone.*

Stability of chloride solutions

Repeated confirmation of the eventual instability of solutions of protactinium in hydrochloric acid, even at 8 N, has been obtained. Such solutions display reproducible properties, in respect of solvent extraction, ion exchange and other chemical

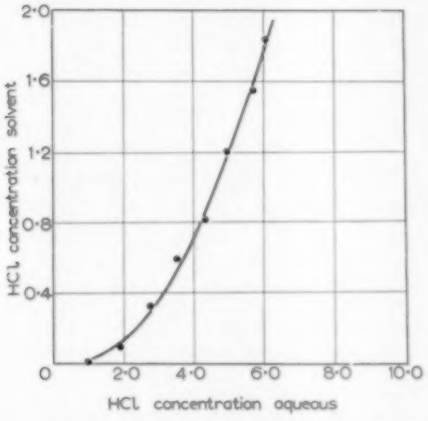

FIG. 11.—Normality of the solvent phase with respect to hydrochloric acid as a function of the concentration of the hydrochloric acid in the equilibrium aqueous phase.

properties, for a number of weeks but eventually a rather rapid change sets in and the protactinium is converted to a colloidal form in a matter of hours. Even the organic extracts show similar behaviour. The lifetime of the solutions appears to be generally greater in polythene than in glass vessels and it is for this reason that the former material is preferred for an extraction process. The data given in Table 1 and Fig. 2 shows that this process produces non-extractable species; there is no evidence for slow processes producing extractable compounds. It has been suggested[45,53] that the polythene vessels used in our previous investigations might contain traces of protactinium complexing agents, such as phosphate esters, which had been added as plasticizers in the fabrication of the polythene. These suggestions appear untenable for the following reasons:

(1) Rapid experiments in glass vessels agreed with the data obtained with the polythene vessels.

(2) Allowing the pure solvent to stand for a week in a polythene vessel gave extraction coefficients lying on the curve obtained when contact only lasted about an hour.

* For the same reason the benzene dilution date protrayed in Graph II in the same paper[3] refers rather to the behaviour of a di-*iso*propyl ketone–di-*iso*propyl carbinol mixture than to the pure ketone, which actually gives a dilution plot with a slope of 5 and not 3 as reported. The correct value is given in the second paper in this series.[1] The latter value is correct for some mixtures of ketone and carbinol. The behaviour of these solvent mixtures will be reported in a subsequent publication.

[45] D. F. PEPPARD, G. W. MASON and M. V. GERGEL, *J. Inorg. Nucl. Chem.* **3**, 370 (1957).

(3) Good reproducibility of results was obtained and wide variations in solvent behaviour encountered.

(4) The variation of extraction coefficient with acid concentration for the solvents does not follow the pattern found for the alkyl phosphoric acids (Fig. 1).

In contrast to the results of PEPPARD *et al.*[45] it was found that the hydrolysed solutions could not be simply reconverted to the extracting form. Two weeks standing in 8 N hydrochloric acid at room temperature, or 30 hr digestion at 90°C, with replacement of lost hydrogen chloride, failed to regenerate more than a fraction of the initially extractable material. A spectrophotometric study of the change in the hydrochloric acid solutions will be reported in a subsequent publication.

All acid solutions containing appreciable quantities of fluoride appear to be thermodynamically stable.

Nature of extracting protactinium compounds

The series of nearly parallel curves shown in Figs. 4, 5 and 6 certainly suggests that the same protactinium compound or compounds are being extracted from the hydrochloric acid solutions by all these ketones. In addition they imply that there are dynamic equilibria operative in the aqueous phase such that an appreciable concentration of these compounds must be present in solutions between 3 and 10N in hydrochloric acid. The anion exchange data confirms that there is an appreciable concentration of chloro-anions of protactinium over the range 4–9 N hydrochloric acid (Fig. 7).

It is unlikely that the pentahalide could be involved to an appreciable extent, not only on account of its ready hydrolysis, but also because it is soluble in carbon tetrachloride which is unable to extract any measurable amount of protactinium from these solutions.

Relatively few cases of solvent extraction from sulphate solution have been described, although the enhancement of extraction from other acids by the addition of sulphuric acid had been reported in a few cases. Polonium and protactinium are amongst the exceptional elements that can be extracted from solutions in this acid.[46] MOORE has published data on the extraction of protactinium from sulphuric acid by di-*iso*butyl carbinol.[47] Our results for methyl *iso*butyl ketone are quite similar. The complete absence of extraction from hydrofluoric acid, even from a 15 N solution, is very interesting in view of the ready extraction of tantalum and the very appreciable extraction of niobium.[41,42]

Factors determining the performance of different solvents

An examination of the performance of the various solvents excluding consideration of those for which mutual solubility effects become important clearly displays the relation between the donor and extracting powers of the solvent. The donor power of such substances is conveniently evaluated by GORDY and STANFORD; base strengths[48] K_B the ratio of the ionisation constant of the solvent considered as a base in aqueous solution to the ionic product of water. This quantity can be

[46] A. CAIRO and A. G. MADDOCK, *Proceedings of the International Conference on Peaceful Uses Atomic Energy, Geneva*, 1955. Vol. 7, p. 331. United Nations (1956).
[47] F. L. MOORE, *Analyt. Chem.* **27**, 70 (1955).
[48] W. GORDY and S. C. STANFORD, *J. Chem. Phys.* **9**, 204 (1941).

estimated from band shifts in the infra-red adsorption spectrum. In Fig. 12 is shown the relation between K_B of the solvent and the activity of hydrochloric acid in the aqueous phase for which the solvent shows an extraction coefficient of one for the protactinium.

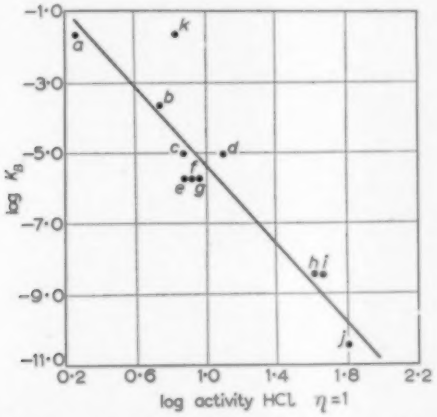

FIG. 12.—GORDY base strength constant plotted as a function of the activity of the hydrochloric acid in the aqueous phase when 50 per cent of the protactinium is extracted.
*a. cyclo*hexanone; *b.* mesityl oxide; *c.* di-*iso*propyl ketone; *d.* di-*iso*butyl ketone; *e.* di-ethyl ketone; *f.* acetophenone; *g.* methyl *n*-hexyl ketone; *h. o*-nitroanisole; *i. o*-nitrotoluene; *j.* nitrobenzene; *k.* tributylphosphate.

A model for the extraction process

This correlation between the donor and extracting powers of the solvents supplements the evidence of the effects of dilution of the solvent with a neutral diluent and supports the hypothesis that the extracting entity includes molecules of the solvent. The spectroscopic data for ethereal extracts of chloroferric acid are hardly compatible with the coordination of the solvent with the iron.[21] It seems more reasonably to suggest that the solvent is associated with the cationic part of the extracting ion-pair complexes in these systems. This cationic portion may consist either of an aquated solvonium ion $SH^+ \cdot aqS$ or a solvated hydroxonium ion $H_3O^+ \cdot Saq$.* In so far as this model is correct it might be expected that the number of solvent molecules associated with the extracting complex, as determined by the dilution method for a given solvent should be independent of the metal extracted, provided the size of the anionic part of the complex does not change too greatly. It is possible that the two kinds of cationic portion of the extracting complexes, postulated above, are responsible for the appearance of two solvent phases in some systems.[19,49] Thus di-*iso*propyl ether sometimes gives two ethereal phases on extracting an acid solution of ferric chloride.[20] The only analytical difference between these two phases lies in the water/iron ratio.[23] Such a difference would be expected if one phase contained an ion multiplet structure based on solvonium ions and the other contained largely hydroxonium ions.

The model proposed above also predicts that the solvent should show little

* When this manuscript was just completed a copy of *Solvent Extraction in Analytical Chemistry* by G. H. MORRISON and H. FREISER (John Wiley, N.Y. (1957)) was received. A substantially similar model is advanced in this text.

[49] R. DODSON, G. FORNEY and E. H. SWIFT, *J. Amer. Chem. Soc.* **58**, 2573 (1936).

specificity for the extraction of particular complex halo-acids. Again provided that the size of the anionic group does not change too greatly it might be expected that the extracting power of different solvents will vary in the same way for a variety of metals. Unfortunately there are insufficient data yet available to test this prediction very thoroughly, but it is true for at least one pair of metals and a variety

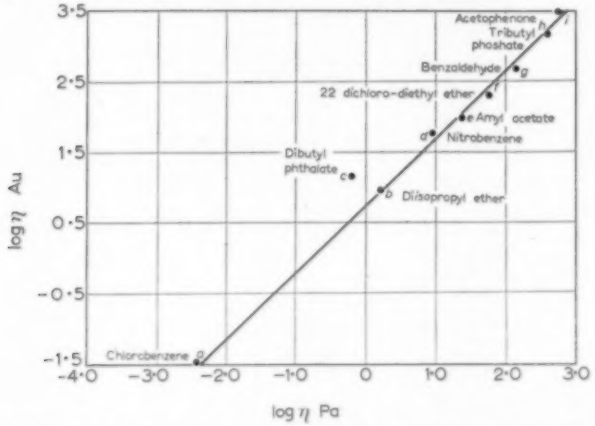

FIG. 13.—Relation between the extraction coefficients of different solvents for gold and protactinium. The former coefficients are taken from the data of the M.I.T. group. All the data refer to measurements from aqueous phases 8 N in hydrochloric acid. The protactinium measurements were made with ^{233}Pa at approximately 5×10^{-10} M.

Solvents:

a. chlorobenzene
b. di-*iso*propylether
c. dibutyl phthalate
d. nitrobenzene
e. amyl acetate
f. $\beta\beta$-dichlorodiethyl ether
g. benzaldehyde
h. tributyl phosphate
i. acetophenone

of solvents. In Fig. 13 the extraction coefficient for protactinium from 8 N hydrochloric acid is plotted against the coefficient for gold from the same aqueous solution and by the same solvents. The gold data are due to IRVINE and SCHONKEN.[50]

The model accounts satisfactorily for the extracting power also depending on the dielectric constant of the solvent. The dependence is more clearly demonstrated when the cationic part of the complex is kept the same, as for instance the alkyl ammonium ion in each of the solutions used for the experiments summarised in Fig. 10. In view of the highly polar character of the extracted complex, and the increase in extracting power with dielectric constant and base strength of the solvent, the question arises as to why extraction from aqueous solutions of such substances takes place at all. The analysis of this problem by FRIEDMAN provides the answer.[21] Extraction only takes place if the complex anion present in the initial aqueous phase is large. The electrostatic contributions to the free energy of transfer of either this anion or the ion-pair acid, or onium salt, to the solvent are generally unfavourable, even with extractants of fairly high dielectric constant. The favourable overall free energy of transfer must arise from the chemical contributions, in particular from the free energy of reformation of the hydrogen bonded water structure in the holes vacated by the anions or ion-pairs and the solvation of the new cationic part of the ion-pairs in the solvent phase.

[50] J. W. IRVINE and P. SCHONKEN, *M.I.T. Progress Report*, November 30, (1955).

The essentially ionic character of the extracted species accounts for a number of the interesting features of solvent extraction from halide solutions. It is known that the extraction coefficient sometimes increases with the concentration of the metal.[49] The increase may arise from the aggregation of the ion pairs in the organic phase, to give triplet, quadruplet, etc., units in the more concentrated solutions. The concentration of metal at which such an effect becomes noticeable should depend on the dielectric constant of the solvent, deviations appearing at lower concentrations with solvents of low dielectric constant. Although this question has not so far been studied systematically, it may be observed that an increase in the extraction coefficient of iron by di-*iso*propyl ether from hydrochloric acid solution can be detected in a concentration range (total Fe^{3+} 0·01–0·5 M) for which the extraction coefficient for $\beta\beta$-dichlorodiethyl ether is constant.[23,51,52] Earlier studies suggested that at the very low end of the concentration range the extraction coefficient was independent of the metal concentration.[53] More recently it has been found that the extraction coefficient may actually be considerably enhanced at very great dilutions,[54–56] and this effect can be attributed to greater ionization in the organic phase at low concentrations. The addition of anions of a strong acid in the solvent phase increases the cation concentration in this phase and thereby reduces the dissociation of the weaker complex halo-acid and hence the extraction coefficient.[57] Thus, the addition of perchlorate, trifluoracetate or nitrate ions to the aqueous phase reduces the anomalously high extraction coefficient shown by gold at great dilutions in hydrochloric or hydrobromic acids. The change in the value of the extraction coefficient upon great dilution of the metal increases with the dielectric constant of the solvent since it will increase with the dissociation constant of the complex halo-acid in the solvent.

The enhanced extraction coefficient found for ^{233}Pa at very low concentration, as contrasted with ^{231}Pa at macroscopic concentration, is clearly shown in the results obtained using nitrobenzene, shown in Fig. 8. When $\beta\beta$-dichlorodiethyl ether, a solvent of lower dielectric constant, is used the enhancement of the extraction at low protactinium concentrations is smaller, although easily measurable. In these examples, it appears that the dependence of the extraction coefficient on the activity of the hydrochloric acid is the same at both concentrations of protactinium. It has been confirmed that the introduction of a strong acid, such as perchloric or trifluoracetic acid progressively reduces the enhanced extraction observed at the low concentrations by a common ion effect in the organic phase.

Quantitative theory

The theoretical treatment of these systems has been discussed by DIAMOND.[58] Unfortunately, even a naive approach ignoring the activity coefficients in the equilibria leads to expressions so complex that, for any other than the simplest

[51] N. H. NACHTREIB and R. E. FRYXELL, *J. Amer. Chem. Soc.* **70**, 3552 (1948).
[52] N. H. NACHTREIB and R. E. FRYXELL, *J. Amer. Chem. Soc.* **74**, 897 (1952).
[53] D. C. GRAHAME and G. T. SEABORG, *J. Amer. Chem. Soc.* **60**, 2524 (1938).
[54] R. H. HERBER, W. E. BENNETT, D. R. BENTZ, L. C. BOGAR, R. J. DIETZ, G. S. GOLDEN and J. W. IRVINE, *Amer. Chem. Soc. Abstr. of Meeting*, Sept., 1954, 33R.
[55] J. SALDICK, *J. Phys. Chem.* **60**, 500 (1956).
[56] C. H. BRUBACKER and C. D. CORYELL, *Amer. Chem. Soc. Abstr. of Meeting*, April, 1956, 44Q.
[57] R. M. DIAMOND, *J. Phys. Chem.* **61**, 69 (1957).
[58] R. M. DIAMOND, *J. Phys. Chem.* **61**, 69 (1957).

example considered by DIAMOND, no explicit expression for the variation of the observed extraction coefficient with the composition of the aqueous phase can be derived. For solvents of moderate or low dielectric constant, dissociation or common ion effects are often negligible at macroscopic concentrations of the extracted metal and the IRVING–ROSSOTTI, treatment is still valid.[9] This is probably true for much of the ^{231}Pa data.

It will be observed, however, in Fig. 8 that the dependence of the extraction coefficient of ^{233}Pa on the concentration of hydrochloric acid in the aqueous phase was the same as for the coefficient for ^{231}Pa at a much higher chemical concentration, even in the moderately ionizing solvent nitrobenzene.

Extraction of thiocyanate complex

The extraction from thiocyanate solutions is not unexpected. Niobium gives a coloured thiocyanate complex that can be extracted into ether.[59,60] The trivalent actinide elements are known to be more strongly complexed by thiocyanate than the lanthanides[61] and DIAMOND has suggested that *f*-orbital participation in bond formation should lead to stronger thiocyanate complexes amongst these elements.[62] The behaviour of the thiocyanate complex is another instance of the surprisingly greater similarity between niobium and protactinium than between tantalum and protactinium.

The significance of the slopes of curves shown in Figs. 4, 5 and 6 will be discussed in a subsequent publication, which will compare these results with similar data for niobium and tantalum.

Acknowledgements—The authors are indebted to the Atomic Energy Research Establishment for a contract covering part of the cost of this investigation, including one of our stipends. (A. G. G.).

[59] I. P. ALIMARIN and R. L. PODVALNAJA, *Zh. anal. khim.* **1** 30 (1946).
[60] C. E. CROUTHAMEL, B. E. HJELTE and C. E. JOHNSON, *Analyt. Chem.* **27**, 507 (1955).
[61] J. P. SURLS and G. R. CHOPPIN, *J. Inorg. Nucl. Chem.* **4**, 62 (1957).
[62] R. M. DIAMOND, Thesis, U.C.R.L. 1434. September 1951.

J. Inorg. Nucl. Chem., 1958, Vol. 7, pp. 113 to 118. Pergamon Press Ltd., London

SOLID STATE AND SOLUTION EXCHANGE OF PLATINUM BETWEEN [Pt(en)Br_4] AND [Pt(en)Br_2]*

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Abstract—Isotopic exchange of platinum between its two states in [Pt(en)Br_2]-[Pt(en)Br_4] was not detected in 24 hr at 25°C. The exchange between the corresponding states in N,N′-dimethylformamide solutions was found to be strongly catalysed by Br^-. A rapid exchange in solution, induced by light, was strongly inhibited by $IrCl_6^{--}$. In the absence of Br^-, an uncontrolled impurity induced an exchange in the dark which prevented reproducible results for solutions made from different solvent batches.

COMPOUNDS of the type PtA_2X_3 (where A is an amine ligand and X is a halogen), in which the average oxidation state of platinum is nominally +3, are well known. The X-ray diffraction structure determination of $Pt(NH_3)_2Br_3$ has been reported by BROSSET.[1] His work showed that [$Pt(NH_3)_2Br_4$] octahedra alternate with [$Pt(NH_3)_2Br_2$] planar squares to form a chain in the direction of one axis of the crystal. Bromine atoms in the octahedra serve as bridging groups in the chains. The intense colour of this compound, and others of its type, is characteristic of many compounds containing one element in two oxidation states.

In the present investigation the isotopic exchange of Pt in solid Pt(en)Br_3 (where en is ethylenediamine) was utilized to ascertain if possibly a single species such as Pt^{III} might exist in the compound or if bromine atoms could rapidly be transferred from Pt^{IV} to Pt^{II}. Since both the synthesis of Pt(en)Br_3 and its dissociation into [Pt(en)Br_2] and [Pt(en)Br_4] must be carried out from solution media, some work was also performed on the corresponding exchange reaction in N,N′-dimethylformamide (hereafter indicated as DMF).

EXPERIMENTAL

Activity

The platinum tracer used in this work was the isotope ^{193m}Pt, prepared by neutron irradiation of platinum metal at the Argonne National Laboratory. An irradiation of the metal prepared from commercial $H_2PtCl_6 \cdot 6H_2O$ yielded about 50 per cent of the total activity as ^{199}Au, formed by the decay of the 31-min ^{199}Pt. This activity was separated from the platinum by dissolution of the metal in aqua regia and repeated extractions of the ^{199}Au into ethyl acetate after the addition of 20 mg of $HAuCl_4$ carrier before each extraction. Also, an additional large fraction of activity followed iridium in the separation scheme as devised by GILCHRIST and WICKERS.[2] Although a single separation removed a large fraction of the iridium activity, an inconveniently large fraction of the ^{192}Ir activity persisted in the sample despite repeated applications of this procedure. Consequently, subsequent activities were obtained by irradiation of platinum metal prepared from K_2PtBr_6 which had been

* Contribution No. 568. Work was performed in the Ames Laboratory of the U.S. Atomic Energy Commission.

(1) C. BROSSET, *Arkiv. Kemi. Min. Geol.* **25A**, No. 19 (1948).

(2) R. GILCHRIST and E. WICKERS, *J. Amer. Chem. Soc.* **57**, 2565 (1935).

carefully purified by 3–4 recrystallizations from aqueous solution. Such a procedure effectively eliminated the iridium activity, which was produced by neutron capture of this minor impurity in the irradiated platinum metal. An iridium impurity was also intolerable in another respect, as will be shown in a later section.

Chemicals

K_2PtBr_6. Commercial $H_2PtCl_6 \cdot 6H_2O$ or platinum metal, which had been recovered for re-use and dissolved in aqua regia, was fumed to near dryness 3–4 times with conc. HBr to effect conversion to H_2PtBr_6. K_2PtBr_6 was precipitated by adding a hot solution of KBr to the hot H_2PtBr_6 solution and allowing the mixture to cool slowly. The product was recrystallized 3 times from dilute HBr and dried at 110°C.

$[Pt(en)Br_2]$. The procedure of WATT and MCCARLEY[3] was used for the synthesis of this compound. Further purification was effected by recrystallizing from DMF–ethanol–water solution and drying at 110°C. *Anal.* Calc: for $[Pt(en)Br_2]$:Pt, 47·0. Found: Pt, 47·0.

Solutions of this compound in DMF were found to be stable over long periods of time. Evidence for the stability of such solutions was provided by both spectrophotometric data and the exchange experiments. However, fresh stock solutions were made up for each new batch of solvent DMF. This was necessary since separate batches of DMF frequently gave markedly different exchange rates.

Radioactive $[Pt(en)Br_4]$. After completion of the purification procedure, the platinum activity was converted to K_2PtBr_6 as described above and stored as a stock solution of this salt. Sufficient inactive K_2PtBr_6 was added to an aliquot of the active solution to give the desired quantity of material. The $[Pt(en)Br_4]$ was then prepared by the method given by WATT and MCCARLEY.[3] The product was recrystallized by dissolution in the minimum volume of cold DMF and filtration into an ice-cold mixture containing 50 per cent ethanol, 50 per cent water. After filtration, the orange crystals were washed with ethanol and ether and dried over anhydrous $Mg(ClO_4)_2$. *Anal.* Calc: for $[Pt(en)Br_4]$: Pt, 34·0. Found: Pt, 34·0.

Solutions of this compound were not stable over long periods of time and their ageing was accelerated by light. A spectrophotometric investigation of this ageing effect revealed a slow decrease in the absorption maxima at 373 mμ and 315 mμ on standing in the dark. On exposure to light, especially direct sunlight, the decrease of absorption at these wavelengths was much more rapid. Although the spectrophotometric observations were continued on several solutions during the course of two to three weeks, no new absorption bands appeared in the visible region, even though the bands originally present had faded to a very low absorbance. Neither platinum metal nor any other residue was observed to separate from these solutions. As a result of their instability, solutions of $[Pt(en)Br_4]$ were made up and used within 15 min for a given experiment.

K_2IrCl_6. Chlorine was bubbled through a solution of reagent $IrCl_4$ in dil. HCl in order to assure that all of the iridium was in the +4 oxidation state. The solution was then heated to ca. 90° and the K_2IrCl_6 precipitated by the addition of KCl. After cooling, the crystals were filtered, washed with water and dried at 110°C.

N, N′–*Dimethylformamide*. Reagent grade, commercial solvent was redistilled through a bubble-plate column rated at 60 theoretical plates; only the middle fraction was retained for use in this work. Although the solvent was stored in a tightly capped bottle and was not unduly exposed to the atmosphere, no special precautions were taken to exclude moisture in the preparation of the exchange solutions.

Experimental techniques

Since preliminary experiments indicated that the rate of the exchange reaction was quite sensitive to light, all runs were made in the absence of light except in a few noted instances. The reaction vessels were made from 125 ml Pyrex erlenmeyer flasks. A crease had been pressed into the bottom to provide compartments for the reactants. The flasks were wrapped with black tape to exclude light. Measured volumes of the reactants were pipetted into separate compartments, whereupon the flasks were tightly stoppered and thermostated at the desired temperature for at least 30 min. Exchange was commenced by rocking the flasks to mix the reactants. After the desired time, the exchange was quenched by the addition of 45 ml of diethylether, which precipitated $[Pt(en)Br_2]$ from the mixture.

[3] G. W. WATT and R. E. MCCARLEY, *J. Amer. Chem. Soc.* **79**, 3315 (1957).

In order to improve the filterability of the precipitate, each reaction mixture was allowed to stand 10 min at room temperature before filtration. The precipitate was filtered and washed on tarred filter paper, which had been previously washed and dried under identical conditions. Samples were dried at 100°C for 10 min and weighed after an additional 30 min standing in air. For counting, samples were mounted on an aluminium backing plate, covered with scotch tape, and counted with a γ-ray scintillation spectrometer preset to count only the platinum K X-ray at *ca.* 60 keV.

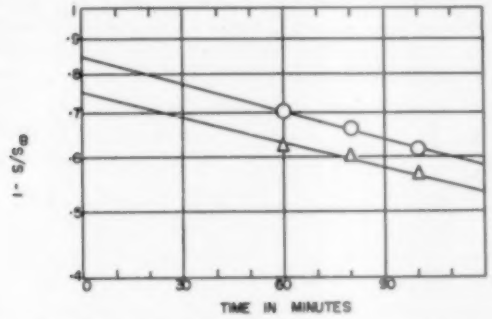


FIG. 1—Solid state exchange experiments. Each curve represents a reaction mixture in which solid Pt(en)Br$_2$ has been dissolved at 0°C to yield a solution $5{\cdot}00 \times 10^{-5}$ M in [Pt(en)Br$_2$] and $2{\cdot}50 \times 10^{-5}$ M in [Pt(en)Br$_4$]. ○–Solution exchange in the presence of solid, inactive Pt(en)Br$_2$ Δ–Exchange curve obtained by dissolution of the solid Pt(en)Br$_2$ tagged with active [Pt(en)Br$_4$]. The time is measured from the addition of Pt(en)Br$_2$ to the solution.

Use of the scintillation spectrometer permitted the detection of any ^{192}Ir in the counting samples by virtue of its several γ-ray peaks. If any of this activity was found to be present, an accurate evalution of its contribution to the counting rate at 60 keV could be made and the appropriate correction applied. However, ^{192}Ir was detected only in samples from the preliminary experiments where the commercial grade of platinum had been used as the source of activity.

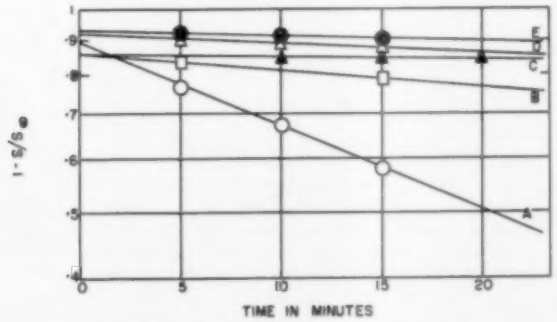


FIG. 2—Effect of light and added reagents on the exchange of platinum between [Pt(en)Br$_2$ and [Pt(en)Br$_4$]. All curves represent runs at 0°C in DMF, $5{\cdot}00 \times 10^{-5}$ M in [Pt(en)Br$_2$] and $2{\cdot}50 \times 10^{-5}$ M in [Pt(en)Br$_4$]. *A*, Diffuse daylight; *B*, Laboratory light at night; *C*, 5×10^{-5} M in Ce(IV); *D*, diffuse daylight and 1×10^{-6} M in K_2IrCl_6; *E*, Dark, no added reagents.

In all exchange experiments the [Pt(en)Br$_4$] initially carried the activity, and the extent of exchange was followed by means of the appearance of activity in [Pt(en)Br$_2$]. Under these conditions the fraction of exchange is defined by the expression $F = S/S_\infty$ where S is the specific activity of platinum in the [Pt(en)Br$_2$] fraction (counts/min mg Pt) at time t, and S_∞ is the specific activity when isotopic equilibrium was established. The exchange reactions were all followed over a period of time so that an exchange curve could be constructed. The experimental data are included in Figs. 1, 2 and 3 in

which log $(1 - F)$ has been plotted as a function of t. The exchange curves showed that separation-induced exchange was not excessive but did amount to 5–17 per cent. However, several points were taken for each curve so that the expected linear relationship[4] could be verified, and the exchange rate could be defined with satisfactory accuracy.

Solid state exchange

Solid $Pt(en)Br_2$[5] was prepared from $[Pt(en)Br_2]$ and tagged $[Pt(en)Br_4]$ under conditions such that the amount of exchange in solution could be estimated before precipitation of the solid. This was done by dissolving 0·2875 g of $[Pt^*(en)Br_4]$ and 0·2076 g of $[Pt(en)Br_2]$ each in 50 ml of DMF and cooling to 0°C, whereupon the two solutions were mixed by stirring for 5 min in the absence of light.

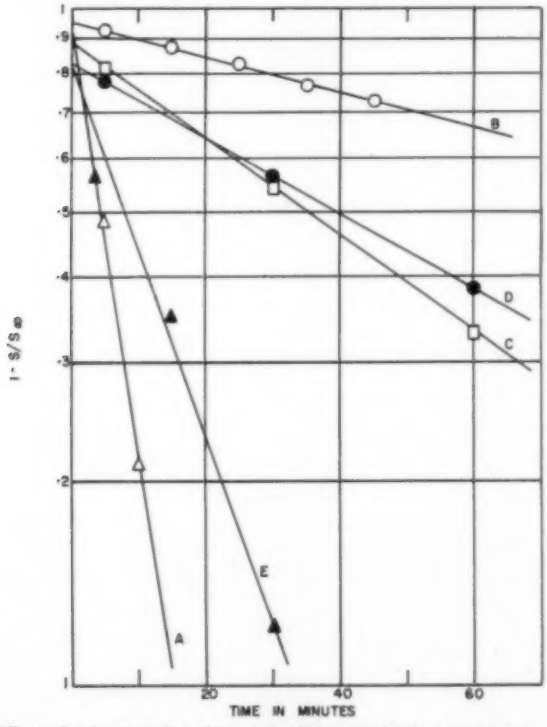


FIG. 3—Effect of solvent and ageing of the $[Pt(en)Br_4]$ solution on the exchange rate. All curves represent DMF solutions $2·50 \times 10^{-3}$ M in $[Pt(en)Br_4]$ and $5·00 \times 10^{-3}$ M in $[Pt(en)Br_2]$ at 25°C. The DMF solvent for *A*, *B*, *D*, *E* is the same for the curves in Fig. 2. *A*, diffuse daylight, *B*, same as *A* but in the dark, *C*, same as *B* but different batch of solvent DMF, *D*, same as *B*, but KBr(10×10^{-3} M) was added.

The concentration of each component, after mixing, was 5·00 mM. $Pt(en)Br_3$ was then precipitated by the addition of 300 ml of 50 v/v aqueous ethanol at 0°C. The crystals were filtered after standing for 15 min, washed with ethanol and ether, and were allowed to stand 24 hr over anhyd. $Mg(ClO_4)_2$.

The components of the active solid were separated by dissolving 99·0 mg in a DMF solution of $[Pt(en)Br_2]$ at 0°C and in the dark such that final concentrations were 5·00 mM $[Pt(en)Br_2]$ and 2·50 mM $[Pt(en)Br_4]$. After allowing 60 min for complete dissolution of the active $Pt(en)Br_3$, aliquots were taken from time to time for precipitation and counting of the $[Pt(en)Br_2]$ in the usual manner. (A preliminary experiment indicated that at least 30 min were required to effect complete dissolution of a similar amount of $Pt(en)Br_3$ at this temperature).

[4] A. C. WAHL and N. A. BONNER (Editors), *Radioactivity Applied to Chemistry* p. 16. Wiley, New York (1951).
[5] G. W. WATT and R. E. MCCARLEY, *J. Amer. Chem. Soc.* **79**, 4585 (1957).

In order to determine the catalytic behaviour of the solid Pt(en)Br$_2$ on the solution exchange, a small sample of inactive Pt(en)Br$_2$ was dissolved in a solution of [Pt(en)Br$_2$] and active [Pt(en)Br$_4$] under the same conditions as above, and samples were removed periodically for counting.

RESULTS AND DISCUSSION

The results of exchange experiments involving the solid green compound Pt(en)Br$_3$ in Fig. 1 show that exchange of platinum between the two components, if it occurs at all, must be very slow at room temperature. The difference in the fraction of exchange between the two experiments (ca. 10 per cent, extrapolated back to the time of the initial contact of the solution with the green compound) can be attributed entirely to the exchange which occurred during the preparation of the active Pt(en)Br$_3$ solid. Therefore no exchange was detected in the solid state over a 24 hr period although a small exchange, up to about 10 per cent, is not excluded because of the uncertainty arising from the separation-induced exchange. Furthermore, a comparison of the results with those from homogeneous solution showed that catalysis of the exchange between [Pt(en)Br$_2$] and [Pt(en)Br$_4$] by the solid Pt(en)Br$_3$ was unimportant. These results clearly indicate that the two platinum species from which Pt(en)Br$_3$ is formed retain their identity during the period of its existence and dissociation, and a common or equivalent state for the platinum does not exist in the compound. Since there is no evidence for the existence of Pt^{III}, a proper formulation for the compound is [Pt(en)Br$_2$]·[Pt(en)Br$_4$]. Very likely the solid possesses a chain structure similar to the one in Pt(NH$_3$)$_2$Br$_3$, which is prepared, however, from the *trans*-compounds. This structure accounts for the stoicheiometry and is consistent with other chemical and physical properties.[5] During the course of this work good single crystals of the green compound, which appear suitable for X-ray diffraction work, were recovered from some of the solutions. Dr. R. E. RUNDLE and his group of this laboratory are investigating the structure of these crystals.

Experiments designed to elucidate the kinetics of exchange in DMF solution were generally hampered by non-reproducibility. Although exchange rates with a single batch of DMF solvent were satisfactorily reproducible, the rates could not be duplicated when different batches of solvent were used. Attempts to further purify the solvent by fairly rigorous procedures failed to eliminate this troublesome factor. Apparently, a trace impurity was capable of catalysing the exchange. However, sufficient purity was achieved that the exchange in the dark was relatively slow as shown in curve *B* of Fig. 3, and an upper limit for a second order rate constant of the exchange may be set as $1{\cdot}33 \times 10^{-2}$ moles^{-1} sec^{-1} at 25°C.

Ageing of the DMF solutions of [Pt(en)Br$_4$] caused an increase in the rate of exchange; e.g. a solution aged in diffuse daylight for one day gave an exchange rate ca. twice that of the fresh solution.

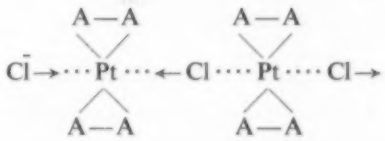
Curve *E* of Fig. 3 demonstrates the effectiveness of bromide in promoting the exchange. WILKINS *et al.*[6] have investigated the rate of the following reaction in the dark by observing the changes in optical rotation:

$$[Pt(l\text{-pn})_2]^{++} + [Pt(en)_2Cl_2]^{++} \rightarrow [Pt(en)_2]^{++} + [Pt(l\text{-pn})_2Cl_2]^{++}$$

where *l*-pn is the ligand *l*-propylenediamine. They found a negligible rate for the reaction in perchlorate solutions, but in the presence of chloride the reaction rate was

[6] R. G. WILKINS, F. BASOLO and R. G. PEARSON, Private communication.

directly proportional to chloride ion concentration, which suggested a transition state:



The similarity of such a system to the present one indicates that the exchange may occur by the corresponding mechanism with Br^- acting in the same fashion as Cl^-. The increase of the exchange rate upon ageing in the present system may result from bromide ion released into the solution by virtue of a solvation process or by the slow reduction of $[Pt(en)Br_4]$. Indeed, the impurity in the solvent may function by means of the release of bromide ion by either a substitution or a reduction step.

The sensitivity of the exchange process to light, on the other hand, probably is not caused by the release of bromide ion since the quantity of Br^- which gave curve *E* of Fig. 3 cannot be released into the solution. These results suggest for the photo-induced process the mechanism proposed by RICH and TAUBE[7] for the $PtCl_4^{--}$ and $PtCl_6^{--}$ exchange reaction

$$[Pt^*(en)Br_4] + h\nu \rightarrow [Pt^*(en)Br_3] + Br$$

$$[Pt^*(en)Br_3] + [Pt(en)Br_2] \xrightarrow{\text{fast}} [Pt^*(en)Br_2] + [Pt(en)Br_3]$$

$$[Pt(en)Br_3] + [Pt^*(en)Br_4] \xrightarrow{\text{fast}} [Pt(en)Br_4] + [Pt^*(en)Br_3]$$

$$[Pt(en)Br_3] + Br \rightarrow [Pt(en)Br_4].$$

Here $[Pt(en)Br_3]$ represents a Pt^{III} species. Further evidence for such a process was provided by the inhibition which a small amount of $IrCl_6^{--}$ in the reaction mixture produced. The $IrCl_6^{--}$ provides a good one-electron oxidation–reduction couple and presumably can inhibit exchange by oxidation of the chain carrier, $[Pt(en)Br_3]$, from the system. Attempts to induce the exchange by the addition of oxidizing agents such as $Fe(CN)_6^{-3}$ or Ce^{IV} were not successful, either because of insufficient solubility in the solvent or oxidation of the solvent.

We wish to acknowledge our appreciation to Drs. BASOLO, WILKINS and PEARSON for providing information about their work prior to publication.

[7] R. L. RICH and H. TAUBE, *J. Amer. Chem. Soc.* **76**, 2608 (1954).

J. Inorg. Nucl. Chem. 1958, Vol. 7, pp. 119 to 128. Pergamon Press Ltd., London

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A CONTRIBUTION TO SODIUM POLYURANATE CHEMISTRY

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Abstract—The preparation of sodium polyuranates by mixing sodium hydroxide solutions with uranyl nitrate and vice versa was studied by potentiometric titration. Points of inflection indicated the presence of polyuranates with different Na : U ratios and of a polyuranate with the empirical formula $(UO_3H_2O)_5N_2O_5$. Polymerization and hydrolysis of uranyl ions in the solution during titration were indicated by changes in the absorption spectra and in pH. Solid polyuranates with empirical formulae $(UO_3H_2O)_5N_2O_5$ and $(UO_3H_2O)_nNa_2O$ were obtained, n having values from 16 to 3. The dependence of the polyuranate composition on the pH of the titration solutions was investigated.

Polyuranates of formulae $(UO_3H_2O)_5N_2O_5$ and $(UO_3H_2O)_nNa_2O$ ($n = 16$ and 5) have similar orthorhombic structures. The unit cell has dimensions $a = 7{\cdot}09 \pm 0{\cdot}02$ Å, $b = 9{\cdot}55 \pm 0{\cdot}02$ Å, $c = 5{\cdot}11 \pm 0{\cdot}06$ Å. The structure of polyuranates with $n < 5$ is different.

THE polyuranates have not hitherto been systematically studied and the acceptable data are not complete.[1–5] WAMSER[6] obtained two polyuranates with the compositions $Na_2U_7O_{22}$ and $Na_6U_7O_{24}$ at pH = 6 and 10 respectively. At these same pH's, points of inflection were obtained on the potentiometric curve during titration of 0·02 N uranyl nitrate, and two different types of crystal-lattice were determined by WAMSER[6] by X-ray diffraction measurements. From phase equilibrium studies of the system UO_3–H_2O–Na_2O at 50°C, RICCI[7] deduced the presence of a compound Na_2O6UO_3 as well as solid solutions of Na_2O in UO_3 with Na : U molar ratios from 8 : 11 to 1 : 3 and from 1 : 12 to 1 : 18. By potentiometric titration GUITER[4] and TRIDOT[8] found the compounds $N_2O_5 5UO_3$ and Na_2O5UO_3. From thermometric titration studies of the system uranyl nitrate–sodium hydroxide, HALDAR[5] deduced the presence of a basic nitrate $4UO_2(NO_3)_2 \cdot UO_2(OH)_2$ and of uranates with the composition $Na_2U_7O_{23}$ and Na_2UO_4. SUTTON[9] obtained some solid polyuranates with compositions $Na_2U_{16}O_{49}$, $Na_2U_7O_{22}$ and $Na_2U_2O_7$.

In this research a study has been made of the formation of sodium polyuranates by measuring their absorption spectra and pH changes during potentiometric titration. Crystal structure and some hydrolytic properties have also been studied for some polyuranates in the solid state.

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(9) J. SUTTON, *J. Inorg. Nucl. Chem.* **1**, 68 (1955).

EXPERIMENTAL

Potentiometric titrations

Potentiometric titrations were carried out with glass-calomel 1 N electrodes. The potential was measured by "Acidimetr" electronic equipment. Fifty millilitres of 0·1 N uranyl nitrate or sodium hydroxide were titrated with 0·1 N sodium hydroxide or uranyl nitrate solutions, and 25 ml 0·1 N uranyl nitrate or sodium hydroxide were titrated with 0·02 N sodium hydroxide or with 0·02 N uranyl nitrate solutions.

Spectrophotometric measurements

Spectrophotometric measurements of the solution during the titration were carried out with recording spectrophotometer SF2 in the 400–600 mμ region. The absorption spectrum was measured at several points on the titration curve.

Diffraction measurements

The X-ray diffraction photographs were obtained in cameras of radius 31·80 mm or 57·16 mm using CuK_α radiation at 30 kV. The exposure time was 3 or 7 hr. The samples were contained in gelatine tubes of 0·6 mm diameter. Correction was made for self-absorption in the sample.

Analytical methods

Uranium was precipitated as $(NH_4)_2U_2O_7$ and weighed as U_3O_8.[10] Sodium was determined as sodium zinc uranyl acetate.[11] Nitrate was determined after reduction to NH_3 by standard methods.[12]

The isolation of the precipitates

The uranyl nitrate and sodium hydroxide solutions were mixed in the required ratio; the precipitate, about 1 g, was centrifuged for 10 min, washed five times by decantation with 10 ml of distilled water and dried at 100°C to constant weight. Since no NaOH was found on washing precipitates of composition $(UO_3H_2O)_5N_2O_5$, we consider the fivefold washing to be satisfactory to remove the adsorbed Na_2O from all the precipitates.

In some cases the precipitates were isolated twice at the same pH; in one case the uranyl nitrate was titrated with the sodium hydroxide solution and in the other the sodium hydroxide was titrated with the uranyl nitrate solution. During a 48 hr period the pH of the solutions was kept constant by adding uranyl nitrate or sodium hydroxide.

RESULTS AND DISCUSSION

Potentiometric titrations

By potentiometric titration of the uranyl nitrate aqueous solution with sodium hydroxide and vice versa potentiometric curves were obtained, two of which are plotted in Fig. 1. Each of the titrations lasted 60 min, so that pH's of 4 to 8 occurred 20 to 40 min after the beginning of the titration.

Curve 1(a) was obtained by titration of uranyl nitrate with sodium hydroxide solution, and curve 1(b) by titration in the reverse direction. Curves 2(a) and 2(b) are the derivatives of these potentiometric curves. The precipitate was formed in the range right of the points *A* and *B* on the titration curves. On the derivative curves, the small inflexion points are visible at different molar Na : U and NO_3 : U ratios. The same potentiometric and derivative curves were obtained in 22 titrations with 0·1 N or 0·02 N solutions under different conditions. The molar NO_3 : U or Na : U ratios (i.e. ratios of NO_3 or Na bonded with U, but not the ratios of total added NO_3

[10] C. J. RODDEN, *Analytical Chemistry of the Manhattan Project* pp. 48, 74, 214. McGraw-Hill, New York (1950).

[11] A. JÍLEK and J. KOŤA, *Vážková analysa a elektroanalysa* Part III, p. 107. SNTL, Prague (1956).

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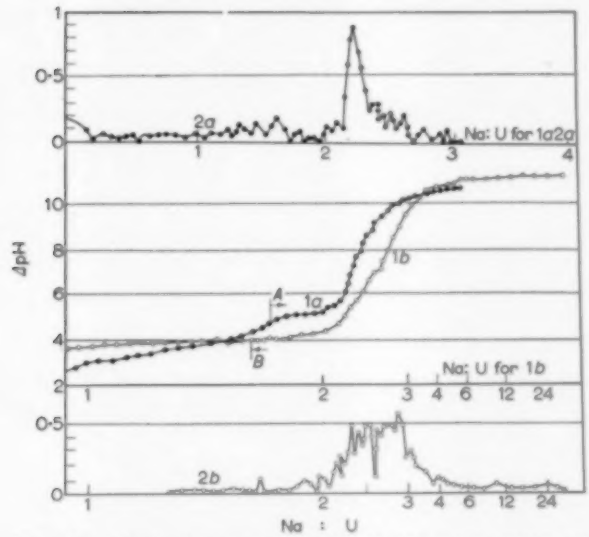

FIG. 1.—Potentiometric titration curves for 0·1 N NaOH and 0·1 N $UO_2(NO_3)_2$ solutions.
Curve 1(a)–Titration of uranyl nitrate by sodium hydroxide
2(a)–Derivative curve of 1(a)
1(b)–Titration of sodium hydroxide by uranyl nitrate.
2(b)–Derivative curve of 1(b).
Points *A* and *B*–The precipitate is formed to the right of *A*, *B*. The molar Na : U ratios are the ratios of total added Na to U.

or Na to U in the mixture) in the solution which correspond to inflexion points on the titration curves are listed in Table 1.

Since the maxima found on the derivative curves were often very small, we have shown in this table only polyuranates observed in at least 70 per cent of the titrations. The molar ratios found were calculated from these measurements, and the spread of values in each case was less than ± 5 per cent.

The precipitate commences to coagulate at a molar ratio $2NO_3$: 5U and all the uranium precipitates at 2Na : 9U ratio. The molar ratios determined from inflexion points on the titration curves show that the –OH or –ONa groups in the chain of the precipitated polyuranate react stepwise with NaOH or $UO_2(NO_3)_2$. Especially

TABLE 1.—INFLEXION POINTS FOUND BY POTENTIOMETRIC TITRATION

Molar ratio found	Observed in % of titrations	Corresponds to the composition of chain unit of precipitate
2Na : 2U	81	$[Na_2O(UO_3H_2O)_2]$
2Na : 3U	81	$[Na_2O(UO_3H_2O)_3]$
2Na : 4U	78	$[Na_2O(UO_3H_2O)_4]$
2Na : 5U	78	$[Na_2O(UO_3H_2O)_5]$
2Na : 6U	78	$[Na_2O(UO_3H_2O)_6]$
2Na : 8U to 9U	74	$[Na_2O(UO_3H_2O)_{8-9}]$
2Na : 16U to 18U	92	$[Na_2O(UO_3H_2O)_{16-18}]$
$2NO_3$: 5U	95	$[(UO_3H_2O)_5(NO_3)_2]$

significant inflexion points are shown by polyuranates with the molar ratios of 2Na : 6U, 2Na : 8U–9U and $2NO_3$: 5U.

Absorption spectra of polyuranates

We prepared various mixtures of 0·1 N solutions of uranyl nitrate and sodium hydroxide and measured their pH and absorption spectra after precipitation, during half an hour after mixing. These are similar conditions to those of the titration. We repeated the measurements after 1, 8 and 30 days to find their dependence on the time of standing.

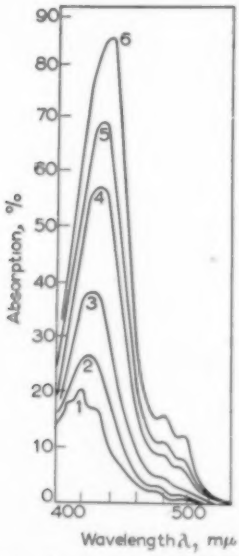

FIG. 2.—The absorption spectra of $NaOH–UO_2(NO_3)_2$ solutions.

Curve	1	2	3	4	5	6
Corresponds to Na : U ratio	0 : 1	0·270 : 1	0·576 : 1	0·96 : 1	1·15 : 1	1·46 : 1

The curves were measured direct after preparation of mixtures in a 2 cm cell.

The dependence of pH on time was measured for mixtures containing polyuranates of molar ratios $2NO_3$: 5U, ONa : 2U, 2Na : 16U and 2Na : 9U. These polyuranates were prepared from 0·1 N solutions by adding sodium hydroxide to uranyl nitrate. The dependence was also measured for a polyuranate of molar ratio 2Na : 8U, which was prepared by adding 0·1 N uranyl nitrate to 0·1 N sodium hydroxide. From the results obtained it is evident that there is a rather quick decrease of pH after adding sodium hydroxide to uranyl nitrate solution during the first day, of about one unit of pH. This decrease is apparently caused by stepwise progress of the neutralization reaction. On adding a solution of uranyl nitrate to sodium hydroxide the inverse process was not observed.

Absorption spectra of solutions of various Na : U ratios, separated from the precipitate during potentiometric titration, are plotted in Figs. 2 and 3. From all of these spectra it is evident that with increasing Na : U ratio of the mixed solution the peak of the absorption curve increases and shifts from 419 mμ to 438 mμ. Then the absorption shifts insignificantly back to the lower wavelengths, splits into two

absorption maxima (426 mμ and 435 mμ), and increases up to a molar ratio of $2NO_3$: 5U in the solution. Then the peaks decrease and precipitation of uranium occurs (curve No. 10).

According to SUTTON's[13] calculations the absorption at 426 mμ and 435 mμ corresponds to the $[U_3O_8]^{++}$ ions. According to curve 14 the maximum absorption of dissolved polyuranate, of composition $(UO_3H_2O)_5N_2O_5$, also lies in the range 424–434 mμ. On standing, the absorption changes systematically. Spectra of mixtures with lower content of sodium, where precipitation during standing does not occur, assume in the course of time the shape of spectra with higher content of sodium directly after mixing. All these facts indicate the progressive polymerization of uranyl ions in solution.

Solid polyuranates

The solid polyuranates were preparated as described below and analysed for Na, U and NO_3. The water content was calculated by difference between the sum of $Na_2O + N_2O_5 + UO_3$ and the total weight of sample. The dependence of the Na : U ratio of these samples on pH of solutions is illustrated in Fig. 4.

The results obtained on adding NaOH to solution of uranyl nitrate are indicated by ○ (molar composition of precipitates—curve 1) and by ⊡ (initial molar composition of polyuranate in solution calculated from composition of reaction mixture—curve 3). The results obtained by adding uranyl nitrate to sodium hydroxide solution are indicated by ⊗ (molar composition of precipitates—curve 2) and by ⊠ (initial molar composition of polyuranate in solution similarly to curve 2—curve 4).

It is evident from Fig. 4 that the curves 1 and 2, expressing the relation between pH and precipitate composition, are approximately parallel. By comparison of curves 1 and 3 with the analogous pair 2 and 4 (Fig. 4) it follows that the precipitates obtained by titration with sodium hydroxide have higher Na : U molar ratios than they could have in the solution immediately after mixing. On the other hand, the precipitate obtained by titration with uranyl nitrate solution always has a Na : U ratio close to that of the solution. If the mixture is left to stand for several hours with the precipitated solid, the precipitate becomes enriched in sodium. Its composition approaches to that lying on the lower curve 2. These experiments are indicated by points ○ and × (Fig. 4); the separation was carried out after 48 hr standing. During this time the acidity was adjusted three times to pH = 8 and after 48 hr it was estimated that no further change occurred. Therefore the lower curve 2 indicates the approximate composition of precipitates in dependence on pH after reaching equilibrium in the solution.

It is evident from these results that slow reaction causes hydrolytic precipitation and successive neutralization of the precipitate. The composition of these precipitates depends (from Fig. 4) on the pH, on the method of preparation and on the time of contact of the precipitate with the solution. With increasing time of contact, the hydrolytic reaction of precipitate with the solution reaches equilibrium. At the same time, the precipitated polyuranate can be slowly enriched in sodium by contact with solution of higher pH. In contact with solution of lower pH the precipitate can be reduced in sodium. Therefore it is possible to change the sodium content in the solid polyuranate by changing the pH of the solution. These experiments lead to the

[13] J. SUTTON, *Report NRC*–1612 (March 1947).

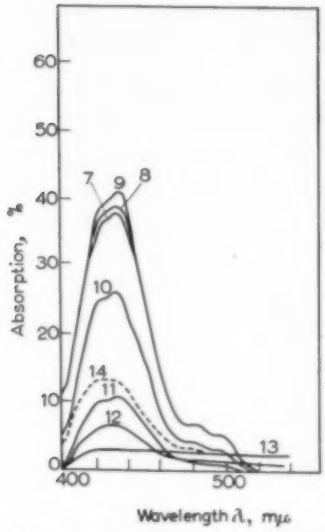

FIG. 3.—The absorption spectra of NaOH–$UO_2(NO_3)_2$ solutions.

Curve	7	8	9	10	11	12	13
Corresponds to Na : U ratio	1·50 : 1	1·54 : 1	1·61 : 1	1·73 : 1	1·92 : 1	2·11 : 1	2·23 : 1

Curve 14 shows the absorption spectrum of dissolved compound $(UO_3 \cdot H_2O)_5 \cdot N_2O_5$.
The curves were measured immediately after preparation of mixtures in a 1 cm cell (7–11) or a 2 cm cell (12–14).

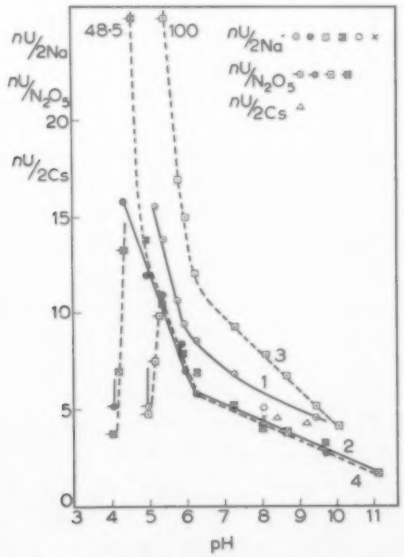

FIG. 4.—The dependence on pH of the composition of the precipitates and solutions.
Curve 1–Composition of precipitates prepared by adding NaOH to $UO_2(NO_3)_2$–points ○.
2–Composition of precipitates prepared by adding $UO_2(NO_3)_2$ to NaOH–points ⊗.
3–Calculated composition of solutions prepared by adding NaOH to $UO_2(NO_3)_2$–points ⊡.
4–Calculated composition of solutions prepared by adding $UO_2(NO_3)_2$ to NaOH–points ⊠.
Points ○ and × –Composition of precipitates after 48 hr standing and adjusting pH to 8.
Points △–KOUŘÍM's[14] experiments.

conclusion that polyuranates behave like cation exchangers in the pH range 4·5–11.

This conclusion for sodium confirms the experiments of KOUŘÍM,[14] who prepared the polyuranates of caesium by mixing uranyl nitrate solution at various pH's with caesium hydroxide, traced by ^{137}Cs. His results lie in the range between curves 1 and 2 (Fig. 4) where they are indicated by points △, and show roughly the validity of our conclusions for Cs also. Further KOURÍM[14] demonstrated that caesium, bound as polyuranate, is washed out with 0·62 M ammonium nitrate neutralized to pH = 8. This fact confirms the exchange property of polyuranates for the alkali metals.

Finally it has been ascertained that the majority of samples of uranates contain one molecule of water to one molecule of UO_3 (Table 2).

TABLE 2.—WATER CONTENT OF POLYURANATES

Ratio found in precipitate	Calculated ratio U : H_2O	
	Titration with 0·1 N sodium hydroxide	Titration with 0·1 N uranyl nitrate
$2NO_3$: 5U	5U : 5·25H_2O	5U : 4·7H_2O
2Na : 16U	16U : 15·3H_2O	16U : 34H_2O
2Na : 14U	14U : 13·7H_2O	—
2Na : 11U	11U : 10·3H_2O	—
2Na : 7U	7U : 6·55H_2O	—
2Na : 6U	—	6U : 6H_2O
2Na : 5U	5U : 4·9H_2O	5U : 7·4H_2O
2Na : 3U	—	3U : 3H_2O

From the table and from the preceding results it follows, that the elementary chain unit of polyuranates is of composition $[Na_2O(UO_3H_2O)_n]$, where n varies from 16 to 2.

Crystal structure of polyuranates

Interplanar distances d of diffraction patterns were calculated from our X-ray photographs and compared with WAMSER's[6] data. We found that the diffraction patterns of polyuranates of composition ratios $2NO_3$: 5U, 2Na : 16U and 2Na : 5U are identical and the d values agree with those of WAMSER's structure *A*. Polyuranate of composition ratio 2Na : 3U, whose values of d are given in the second column of Table 3 has a different structure, designated by WAMSER[6] as structure *B*. The third column of Table 3 contains WAMSER's values of d for structure *B* which he found for polyuranates of ratio 2Na : 3U and for other higher ratios. From the foregoing measurements it is evident, in accord with WAMSER, that there are two different polyuranate structures *A* and *B*. Structure *A* is valid for mole ratios from $2NO_3$: 5U to 2Na : 5U, whereas polyuranates of mole ratios greater than 2Na : 5U (e.g. 2Na : 3U) have structure *B*. WAMSER has found structure *B* also for a mole ratio of 6Na : 7U.

Indexed values of $1/d^2$ for structure *A* are given in Table 4. Fair agreement was found for 53 observed and calculated $1/d^2$ values for an orthorhombic lattice, with parameters $a = 7{\cdot}09 \pm 0{\cdot}02$ Å, $b = 9{\cdot}55 \pm 0{\cdot}02$ Å, $c = 5{\cdot}11 \pm 0{\cdot}06$ Å, obtained as

[14] V. KOUŘÍM, Private communication.

the mean of three measurements. The density of polyuranate with formal formula $(UO_3H_2O)_{11}Na_2O$ was determined pycnometrically in ethanol as 5·7 g/cm³. The X-ray density with 4U in the unit cell was found to be 5·94 g/cm³.

The lattice parameters for pure UO_3H_2O are: $a = 6{\cdot}87$ Å, $b = 4{\cdot}28$ Å, $c = 10{\cdot}21$ Å, and its X-ray density is 6·73 g/cm³.[15] By comparison it is evident that the density of $(UO_3H_2O)_{11}Na_2O$ is lower than that of UO_3H_2O, so the lattice is less

TABLE 3.—INTERPLANAR DISTANCES d FOR STRUCTURE B

Pattern intensity	d found	WAMSER's[6] d
1. s.	5·843	6·06
2. m.s.	4·136	
3. v.s.	3·397	3·42
4. s.	3·200	3·25
5. v.w. diffuse	2·985	3·02
6. v.w.	2·699	2·74
7. v.w.	2·505	
8. v.w.	2·260	
9. s.	1·985	2·01
10. s.	1·888	1·91
11. w. diffuse	1·729	1·72
12. w. diffuse	1·417	1·66
13. v.w. diffuse	1·352	
14. v.w. diffuse	1·288	
15. v.w. diffuse	1·123	
16. v.w. diffuse	1·070	

v.s.–very strong s.–strong m.s.–moderate strong w.–weak v.w.–very weak

close-packed. The quantity of Na_2O can vary in the range corresponding to $(UO_3H_2O)_nNa_2O$ with n lying between 5 and 16 without changing the lattice parameters. For $n = 8$, the ratio in the unit cell is 1 Na to $4(UO_3{\cdot}H_2O)$ and it can be assumed that for $n = 8$ sodium probably occupies a special structural position. Also the potentiometric titration curve shows for $n = 8$ a significant inflexion point.

CONCLUSIONS

The reaction mechanism during titration of dilute solutions of uranyl nitrate with sodium hydroxide can be understood as follows: on addition of small amount of sodium hydroxide to uranyl nitrate solution a series of ions is formed of polymer form $[UO_2(UO_3H_2O)_n]^{++}$; this agrees with AHRLAND *et al.*[1] The precipitate prepared at pH = 4 has a structure *A* and the composition of its chain unit is $[(UO_3H_2O)_5N_2O_5]$. By further addition of sodium hydroxide it loses N_2O_5 and $[(UO_3H_2O)_nNa_2O]$ is formed. The value of n in this precipitate changes continually with pH from $n = 16$ to $n = 5$. Between $n = 5$ and $n = 3$ the lattice changes from structure *A* to structure *B*. According to WAMSER[6] and BACHELET[2] this structure remains unchanged until the final composition $Na_2U_2O_7$ is reached.

[15] G. T. SEABORG and J. J. KATZ, *The Actinide Elements* p. 175. McGraw-Hill, New York (1954).

TABLE 4.—INDEXED *hkl* VALUES FOR STRUCTURE *A*

Pattern intensity	$1/d^2$ found	$1/d^2$ calculated	*hkl*
1. v.s.	0·0195	0·0197	100
2. v.w. diffuse	0·0504	0·0486	011
3. v.w.	0·0570	0·0576	101
4. v.s.	0·0793	0·0790	200
5. v.s.	0·0828	0·0815	021
6. v.w.	0·0907	0·0899	210
7. v.s.	0·0978	0·0986	030
8. v.s.	0·1006	0·1012	121
9. v.w. diffuse	0·1357	0·1363	031
10. s. diffuse	0·1523	0·1508	002
11. s. diffuse	0·1559	0·1560	131
12. v.w.	0·1698	0·1705	102
13. v.w.	0·1879	0·1886	310
14. v.w.	0·2167	0·2154	301
		0·2173	231
		0·2156	122
15. v.w.	0·2318	0·2298	202
		0·2327	141
16. m.s.	0·2408	0·2408	212
17. w.	0·2495	0·2494	032
18. w.	0·2585	0·2592	321
19. v.w.	0·2776	0·2763	330
		0·2746	050
20. v.w. diffuse	0·3155	0·3160	400
21. w.	0·3303	0·3284	232
		0·3288	302
22. v.w. diffuse	0·3440	0·3458	142
23. v.w. diffuse	0·3616	0·3598	420
		0·3591	103
24. w. diffuse	0·3834	0·3832	023
25. v.w. diffuse	0·3892	0·3907	341
		0·3908	251
26. w. diffuse	0·4021	0·4029	123
27. w.	0·4773	0·4777	412
28. v.w.	0·4934	0·4940	500
29. v.w.	0·5433	0·5421	511
30. v.w.	0·5570	0·5562	170
31. v.w.	0·5885	0·5898	450
32. w.	0·6075	0·6035	004
		0·6099	361
33. v.w.	0·6359	0·6341	114
34. v.w.	0·6551	0·6554	403
35. v.w.	0·6841	0·6825	204
36. v.w.	0·7097	0·7070	172
		0·7105	460
		0·7110	600
37. v.w.	0·7915	0·7925	621
38. v.w. diffuse	0·8262	0·8250	324

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TABLE 4—*continued*

Pattern intensity	$1/d^2$ found	$1/d^2$ calculated	*hkl*
39. v.w. diffuse	0·8726	0·8727	612
40. v.w. diffuse	0·8984	0·8970	154
41. w.	0·9798	0·9789	710
42. w.	1·049	1·049	721
43. w.	1·067	1·066	730
44. w.	1·120	1·120	305
45. w. diffuse	1·173	1·175	364
		1·174	2 10 0
46. w. diffuse	1·194	1·194	580
47. v.w. diffuse	1·226	1·227	093
		1·227	563
48. v.w. diffuse	1·324	1·324	3 10 2
49. v.w. diffuse	1·333	1·336	065
50. w. diffuse	1·362	1·363	830
51. v.w. diffuse	1·394	1·394	355
52. v.w. diffuse	1·417	1·413	832
		1·419	591
53. v.w. diffuse	1·476	1·477	841

Approximately two hydrogen atoms for every five uranium atoms can be freely exchanged for alkali metal atoms (e.g. Na, Cs), or for the nitrate group, as the pH is varied. During this reaction the orthorhombic lattice of structure *A* remains unchanged.

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ÜBER DIE ELEKTROLYTISCHE ABSCHEIDUNG VON TRÄGERFREIEM STRONTIUM AUS WÄSSRIGER LÖSUNG

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Abstract—The electrolytic deposition of strontium from weak aqueous nitric acid has been investigated. Carrier-free strontium is deposited on the cathode with a yield of 80–90%, when CO_2 is bubbled through a solution of pH value 2·5–6·2.

VOR einiger Zeit haben wir ein Verfahren zur Herstellung von ^{90}Sr–freiem ^{90}Y durch Elektrolyse beschrieben.[1] Trägerfreies Yttrium kann aus einer wässrigen salpetersauren Lösung vom pH-Wert 2,5 mit 90–98% Ausbeute an der Kathode abgeschieden werden. Bei Gegenwart von 5 mg Sr^{2+} in 30 ml Elektrolyt werden etwa 0,5% des Strontiums, entsprechend 20–30 μg, mit abgeschieden. Durch eine mehrfache Wiederholung der Elektrolyse können ^{90}Y-Präparate mit $<10^{-4}\%$ ^{90}Sr erhalten werden.

Die Abscheidung von metallischem Yttrium und Strontium dürfte unter diesen Bedingungen ausgeschlossen sein. Der Einfluss des pH-Wertes auf die Abscheidung des Yttriums spricht dafür, dass die Wanderung zur Kathode als Y^{3+}-Ion erfolgt.[1] In der Nähe der Kathode tritt eine Hydrolyse ein, bedingt durch die Verarmung an H^+-Ionen an der Kathode, die zur Abscheidung von Hydroxyd führt. Die Bildung solcher Hydroxydabscheidungen und das Auftreten von Hydroxydfällungen in der Lösung wurde bei der Elektrolyse wässriger Lösungen von wägbaren Mengen der Seltenen Erden schon vor langer Zeit beobachtet.[2]

Zur Erklärung der Abscheidung des Strontiums haben wir die Bildung von Karbonat in der Nähe der Kathode angenommen. Für diese Annahme sprechen die Beobachtungen von VON BAEYER, HAHN und MEITNER[3] und TOEDT[4], dass Radiumisotope in Gegenwart von kleinen Mengen Bariumträger aus schwach sauren wässrigen Lösungen elektrolytisch abgeschieden werden können, wenn in die Lösung Kohlendioxyd eingeleitet wird. Auch bei der Elektrolyse von radiumhaltigen Bariumsalzen in organischen Lösungsmitteln wurde die Abscheidung von Karbonaten an der Kathode beobachtet.[5,6] Wenn diese Annahme richtig ist, so sollte das Verfahren zur Herstellung von ^{90}Sr-freiem ^{90}Y durch den Ausschluss von Kohlendioxyd während der Elektrolyse verbessert werden können. Zugleich schien eine Möglichkeit gegeben zu sein, Erdalkalielemente auch im trägerfreien Zustand aus wässrigen Lösungen elektrolytisch abzuscheiden, wenn die Lösung laufend mit CO_2 gesättigt wird. Diese Fragen sollten durch die nachstehend beschriebenen Versuche geklärt werden.

(1) G. LANGE, G. HERRMANN und F. STRASSMANN, *J. Inorg. Nucl. Chem.* **4**, 146 (1957).
(2) L. M. DENNIS und B. J. LEMON, *J. Amer. Chem. Soc.* **37**, 131 (1915).
(3) O. VON BAEYER, O. HAHN und L. MEITNER, *Phys. Z.* **16**, 6 (1915).
(4) F. TOEDT, *Z. phys. Chem.* **113**, 329 (1924).
(5) G. VON HEVESY, *Z. Elektrochem.* **16**, 672 (1910).
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EXPERIMENTELLE DURCHFÜHRUNG

Die Durchführung der Elektrolysen und Aktivitätsmessungen wurde bereits beschrieben,[1] so dass hier nur Abweichungen erwähnt werden. Es wurde ein anderes Elektrolysegefäss von 120 ml Inhalt benutzt, das mit einem eingeschliffenen Deckel verschlossen war. Im Deckel waren Öffnungen für die beiden als Elektroden dienenden Platinspiralen und ein Gaseinleitungsrohr angebracht. Es wurden jeweils 80 ml Elektrolyt eingefüllt, dessen Temperatur bei allen Elektrolysen auf 60 ± 5°C gehalten wurde. Die Rührung (ca. 300 Umdrehungen pro Minute) erfolgte wiederum mit der Kathode.

In den erwärmten Elektrolyten wurde Kohlendioxyd oder über Natronkalk gereinigter Stickstoff eingeleitet, ohne dass zunächst an die Elektroden eine Spannung angelegt wurde. Nach einer Stunde wurde die Elektrolyse begonnen, ohne dass der Gasstrom bis zum Ende des Versuchs abgestellt wurde. Bei einigen Versuchen wurde keines der beiden Gase eingeleitet, d.h. unter den bei den früheren Untersuchungen[1] vorliegenden Bedingungen gearbeitet. Es war dabei ohne Einfluss auf die Ergebnisse, ob das Elektrolysegefäss mit oder ohne Deckel verwendet wurde.

Als Indikator wurde bei den meisten Versuchen ^{90}Sr-^{90}Y, bei den restlichen Versuchen ^{89}Sr verwendet. Beide Isotope standen trägerfrei zur Verfügung und wurden sowohl trägerfrei als auch in Gegenwart wägbarer Mengen Sr^{2+} verwendet. Nach der Elektrolyse wurden die Elektroden unter Strom aus dem Elektrolyten gezogen und zunächst dreimal mit Aceton abgespült, dann wurde die Aktivität mit warmer verdünnter Salzsäure abgelöst und 10 mg Sr^{2+}-Träger zugegeben. Wenn ^{90}Sr als Indikator benutzt wurde, erfolgte die Bestimmung der abgeschiedenen ^{90}Sr-Aktivität wie auch die Gehaltsbestimmung der ^{90}Sr-Stammlösung nach Einstellung des radioaktiven Gleichgewichts zwischen ^{90}Sr und ^{90}Y durch Abtrennung und Messung des ^{90}Y. Das ^{90}Y wurde durch karbonatfreies Ammoniak an 5 mg $Fe(OH)_3$ mitgefällt, der Niederschlag wurde nochmals neben 20 mg inaktivem Sr^{2+} umgefällt. Da bei den Elektrolysen nur ein kleiner Teil des ^{90}Sr und der grösste Teil des ^{90}Y abgeschieden wurde—ausgenommen Elektrolysen in CO_2-gesättigter Lösung—wurde der Überschuss an ^{90}Y unmittelbar nach Ende der Elektrolyse durch zwei $Fe(OH)_3$-Fällungen entfernt. Wenn ^{89}Sr als Indikator benutzt wurde, erfolgte die Aktivitätsmessung unmittelbar nach der Elektrolyse durch Fällung mit Soda und Messung des $^{89}SrCO_3$. Der geringe Gehalt an ^{90}Sr-^{90}Y brauchte nicht berücksichtigt zu werden, da ^{89}Sr nur für Versuche in CO_2-gesättigter Lösung verwendet wurde, bei denen der grösste Teil des Strontiums abgeschieden wird. Weitere Einzelheiten über die Aktivitätsmessungen wurden früher beschrieben.[1]

Die Lösungen mit verschiedenem pH-Wert wurden aus Salpetersäure und Ammoniak durch Verdünnen hergestellt. Bei einigen Versuchen wurde eine verdünnte Salpetersäure vom pH-Wert 2,5 benutzt, die mehrere Stunden im Stickstoffstrom ausgekocht worden war und in einer Flasche aufbewahrt wurde, die mit einem Natronkalkrohr verschlossen war.

Die in den Tabellen angegebenen Fehlergrenzen ergaben sich aus den Abweichungen mehrerer Parallelversuche. Wenn die Parallelversuche gut übereinstimmten, wurde ein Mindestfehler von ±5% angenommen.

ERGEBNISSE UND DISKUSSION

Einfluss des CO_2-Gehaltes. Tabelle 1 gibt die Resultate einer Versuchsreihe, bei der die Elektrolyse bei einem pH-Wert von 2,5, d.h. unter den für die ^{90}Y-Abtrennung optimalen Bedingungen,[1] durchgeführt wurde. Durch Einleiten von Kohlensäure oder Stickstoff wurde der CO_2-Gehalt des Elektrolyten verändert. Die "ohne Gas" durchgeführten Versuche entsprechen den in der früheren Untersuchung mitgeteilten, wobei allerdings das Volumen des Elektrolyten (80 ml statt 30 ml), die Klemmenspannung (18 statt 12 Volt) und die Stromdichte (30–40 statt 20–25 mA/cm²) verändert wurden. Alle in der Tabelle angegebenen Werte sind Mittelwerte aus mindestens drei Versuchen.

Bei den Versuchen wurden teilweise erhebliche Schwankungen in der Strontiumabscheidung beobachtet, die die Auswertung erschweren. Die Tabelle zeigt, dass die Abscheidung des Strontiums aus einer CO_2-gesättigten Lösung mit recht guter Ausbeute möglich ist. Dagegen ist es ohne wesentlichen Einfluss, ob die Elektrolyse

TABELLE 1.—AUSBEUTE BEI DER KATHODISCHEN ABSCHEIDUNG VON STRONTIUM BEI EINEM pH-WERT VON 2,5

Sr^{2+}-Träger (mg/80 ml)	trägerfrei	0,1 mg	10 mg	10 mg
Spannung (Volt)	18V	18V	18V	12V
Stromdichte (mA/cm^2)	30–40	30–40	30–40	15–20
Dauer der Elektrolyse	2h	2h	2h	1h
N_2-Strom*	2,5 ± 0,4%	0,2 ± 0,1%	0,2 ± 0,1%	0,02 ± 0,01%
N_2-Strom†		0,3 ± 0,1%	0,3 ± 0,2%	0,05 ± 0,03%
ohne Gaseinleiten†		0,9 ± 0,4%	0,3 ± 0,2%	0,05 ± 0,02%
CO_2-Strom†	70 ± 5%	62 ± 18%	65 ± 3%	29 ± 4%

* Elektrolyt im N_2-Strom ausgekocht
† Elektrolyt nicht ausgekocht

unter Luftzutritt erfolgt oder ob die Aufnahme von Kohlensäure durch die Lösung verhindert wird. Es ist damit nicht möglich, die Abscheidung kleiner Mengen Strontium bei der elektrolytischen Abtrennung von ^{90}Y aus ^{90}Sr auf die Anwesenheit von CO_2 in der Lösung zurückzuführen. Ebensowenig ist es möglich, das Verfahren zur Darstellung des ^{90}Y durch den Ausschluss von CO_2 bei der Elektrolyse zu verbessern. Die Verminderung der Abscheidung bei verminderter Stromdichte (letzte Spalte der Tabelle 1) ist für die präparative Darstellung von reinem ^{90}Y ohne Interesse, da zugleich die Ausbeute an ^{90}Y auf etwa 50% sinkt.

Ohne weitere Versuche kann keine Erklärung für die Ursache der Strontiumabscheidung gegeben werden. Es liegt nahe, eine Adsorption zu vermuten, da die abgeschiedene Menge bei Konzentrationen von 0,1 bzw. 10 mg Sr^{2+}/80 ml ungefähr der Konzentration proportional ist. Da jedoch im zweiten Fall immerhin 20 μg Strontium abgeschieden wurden und die Elektrodenoberfläche etwa 3 cm^2 betrug, muss die Kathode von mehreren Schichten einer Strontiumverbindung bedeckt worden sein. Dadurch scheidet eine rein adsorptive Abscheidung aus.

Abscheidung von trägerfreiem Strontium. Tabelle 1 zeigt, dass in CO_2-gesättigter Lösung auch trägerfreies Strontium mit recht guter Ausbeute abgeschieden werden kann. Da eine solche Abscheidung für manche Zwecke interessant sein mag, wurden die günstigsten Bedingungen durch eine weitere Versuchsreihe untersucht. Die Ergebnisse sind in Tabelle 2 zusammengestellt; alle Werte sind Mittelwerte aus

TABELLE 2.—AUSBEUTE BEI DER KATHODISCHEN ABSCHEIDUNG VON TRÄGERFREIEM STRONTIUM AUS CO_2-GESÄTTIGTER LÖSUNG

pH-Wert*	1,1	2,5	4,2	6,2	7,9
Dauer der Elektrolyse					
10 min		62 ± 3%	26 ± 3%	43 ± 3%	
30 min		84 ± 6%	33 ± 4%	90 ± 5%	
60 min		68 ± 7%	66 ± 3%	88 ± 4%	
120 min	4 ± 2%	78 ± 8%	73 ± 5%	89 ± 4%	7 ± 2%

* Angegeben ist der vor dem Einleiten des CO_2 eingestellte pH-Wert. Der pH-Wert bleibt im pH-Bereich 1,1–4,2 bis zum Ende der Elektrolyse konstant, bei den pH-Werten 6,2 und 7,9 sinkt er dagegen durch das Einleiten von CO_2 bis zum Beginn der Elektrolyse (1 Std. später) auf 4,9 bzw. 5,2 ab und bleibt dann konstant.

mindestens zwei Versuchen. Alle Elektrolysen wurden bei 60°C, 18 Volt Spannung und 40 mA/cm² Stromdichte durchgeführt.

Die Tabelle zeigt, dass der pH-Wert bei 1–2 stündiger Elektrolyse keinen wesentlichen Einfluss auf die Ausbeute hat, wenn im pH-Bereich 2,5–6,2 gearbeitet wird. In stärker saurer oder alkalischer Lösung findet dagegen keine Abscheidung statt. In dieser Hinsicht liegen ähnliche Verhältnisse vor wie bei der Abscheidung von trägerfreiem Yttrium. Dagegen ist der Einfluss des pH-Wertes auf die Abscheidungsgeschwindigkeit nicht so eindeutig wie beim Yttrium. Die günstigsten Bedingungen für die Strontiumabscheidung liegen nach Tabelle 2 bei einem pH-Wert von 6,2, der sich durch das Einleiten des CO_2 vor der Elektrolyse auf etwa 5,0 erniedrigt. Unter diesen Bedingungen ist eine 30 Minuten dauernde Elektrolyse ausreichend.

Die anodische Abscheidung ist bei zweistündiger Elektrolyse im pH-Bereich 2,5 bis 6,2 gering und beträgt $2 \pm 1\%$; eine Abhängigkeit vom pH-Wert war nicht eindeutig zu erkennen.

Der Mechanismus der kathodischen Abscheidung von Strontium in CO_2-gesättigter Lösung dürfte ähnlich dem für die Abscheidung von Yttrium angenommenen sein: Der Transport zur Kathode erfolgt als Sr^{2+}, während in der Nähe der Kathode durch die Verarmung an H^+-Ionen und die Anwesenheit von HCO_3^- und CO_3^{2-}-Ionen die Bildung und Abscheidung von $SrCO_3$ möglich wird. Zu hohe H^+-Ionenkonzentration verhindert die Abscheidung, während in alkalischer Lösung der Transport zur Kathode durch Bildung von Radiokolloiden oder andere Effekte behindert wird. Man kann annehmen, dass auch andere Erdalkalielemente, vor allem aber Barium und Radium, unter gleichen Bedingungen trägerfrei abgeschieden werden können.

Herrn Prof. Dr. F. STRASSMANN danke ich für sein Interesse, Herrn A. KUNTZ für seine Hilfe bei der Durchführung der Untersuchung. Der DEUTSCHEN FORSCHUNGSGEMEINSCHAFT bin ich für die Bereitstellung des bei der Untersuchung benutzten Strahlungsmessgerätes zu Dank verpflichtet.

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PRODUCTION DE ^{131}I SANS PORTEUR A PARTIR D'ACIDE TELLURIQUE

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Abstract—The described method uses telluric acid (H_6TeO_6) as a target for the production of ^{131}I in nuclear reactors. The performed experiments indicate that it is sufficient to dissolve the target in water in presence of a strong acid and to distil in order to carry over the iodine as I^- and I_2.

The method eliminates the difficulties of target dissolution and makes it possible to obtain a very pure distillate after an easily performed separation. It is possible to use the sulphuric and phosphoric acids indefinitely but an excess of either acid increases the distillate acidity.

The irradiations were carried out in the BR 1 reactor at Mol in a thermal flux of about 10^9 to 2×10^{13} neutrons/cm²/sec in temperature conditions never exceeding 90°C.

The valency-state of the distilled iodine seems to be independent of the flux and of the integrated flux to which the target is submitted.

Apparatus and production method are described.

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TOUTES les méthodes de production de ^{131}I par voie humide[1–7] ont, pour point de départ, l'irradiation de tellure élémentaire. Cette cible nécessite une attaque sulfochromique extrêmement brutale qui transforme le tellure en tellurate et l'iode en iodate. La réduction par l'acide oxalique qui fait suite à cette opération transforme les tellurates en tellurites, tandis que l'iode est réduit à l'état élémentaire. La distillation conduit en général à des distillats trop impurs pour être directement utilisés en médecine.

KENNY et SPRAGG[3,7] sont parvenus à réduire la quantité d'impuretés entraînées en utilisant une quantité minimum d'acide oxalique mais les acidités des distillats restent importantes.

En utilisant l'acide tellurique comme cible, on évite une dissolution dangereuse et la nécessité d'une réduction qui augmente les risques de présence d'impuretés dans les distillats. Les rendements obtenus en ^{131}I sont satisfaisants.

DISCUSSION

Principe de la méthode

Il est bien connu que l'irradiation du tellure naturel par les neutrons lents conduit aux isotopes 127, 129 et 131 qui apparaissent chacun dans deux états isomères. Ces divers tellures conduisent, par désintégration β^- à l'iode-127, 129 et 131.

^{127}I est stable et ^{129}I est de trés longue vie; ^{131}I est donc le seul isotope de l'iode utilement formé.

[1] M. D. KAMEN, *Radioactive Tracers in Biology*. Academic Press Inc., New York (1947).
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[6] K. TAUGBOLL and ULF BLIX, *Production of ^{131}I for medical use from tellurium irradiated in the uranium pile at Kjeller Jener* 18 (Norway) (1953).
[7] A. W. KENNY and W. T. SPRAGG, *AERE/C/R*-349 (1957).

Lorsqu'on irradie de l'acide tellurique (H_6TeO_6), les essais que nous avons réalisés prouvent qu'il suffit de dissoudre la cible dans de l'eau bidistillée en présence d'acide fort et de distiller pour entrainer l'iode sous forme de I^- et I_2. Les principaux avantages de la méthode sont:—

la facilité de purification d'une cible soluble dans l'eau, ce qui permet l'obtention de solutions actives finales très pures, la facilité de séparation de l' ^{131}I, l'élimination de tous les réactifs nécessaires à la dissolution du tellure qui sont toujours susceptibles d'être entraînés dans les distillats, l'élimination de l'acide oxalique, donc des possibilités d'entraînement de cet acide et de ses produits de décomposition.

Activation de la cible

On peut calculer l'activité obtenue en appliquant l'équation suivante:

$$A^{131I} = 10^{-12}\,\phi\,(20{\cdot}07 - 0{\cdot}64e^{-0{\cdot}0231t} - 9{\cdot}94e^{-1{\cdot}6632t} - 9{\cdot}94e^{-0{\cdot}0036t})$$

équation dans laquelle:

A = millicuries d'iode-131 par gramme de tellure élémentaire naturel irradié.
t = temps d'irradiation en heures.
ϕ = flux exprimé en neutrons/cm²/sec.

Cette équation nous permet de voir que si l'on irradie 150 g d'acide tellurique pendant 14 jours dans un flux de 10^{12} neutrons/cm²/sec, on peut donc atteindre une activité d'environ 1400 millicuries de ^{131}I.

Appareillage de comptage et de mesure

Les comptages ont été effectués soit à l'aide d'un compteur Geiger (fenêtre de 1·9 mg/cm²) soit à l'aide d'un scintillateur creux du type "Well". Les rendements se situaient respectivement aux environs de 10·4 et de 53·4 pour cent.

On a utilisé indifféremment l'un ou l'autre type de comptage pour les mesures relatives qui importaient ici. Seul, le niveau de l'activité à mesurer est intervenu. La spectrométrie γ a été réalisée à l'aide de cristaux de NaI $2'' \times 2''$ et NaI Well $2'' \times 2''$. Les impulsions furent analysées avec le "256 channel analyser" RCL mark 20 type Argonne, modèle 2603[8].

Matériel et produits

Pour les essais préliminaires de mise au point de la méthode de production proprement dite, on a utilisé un appareil simple constitué par un ballon de deux litres relié à un réfrigérant, muni d'une corne par l'intermédiaire d'un dôme. Nous avons utilisé:—l'acide tellurique (H_6TeO_6) s/c BDH Analar, l'acide sulfurique (d. 1·84) Merk n° 731, H_2O bidistillée dans le quartz.

Irradiations

Les irradiations ont été effectuées dans BR 1, dans des flux thermiques allant de 10^9 à 2×10^{12} neutrons/cm²/sec. Les échantillons enfermés de façon classique dans des bôites d'aluminium, furent placés dans un endroit approprié au flux désiré mais toujours entourés de graphite. Dans ces conditions, la température n'excèda jamais 90°C.

[8] R. N. SCHUMANN and J. P. MACMAHON, *Rev. Sci. Instrum.* **27**, 675 (1956).

RÉSULTATS

Influence du pH sur la vitesse de distillation

On a constaté comme il faut s'y attendre, que pour obtenir une bonne distillation, on doit opérer en milieu acide. Ceci conditionne l'emploi d'un acide fort, fixe et non entraînable à la vapeur. On a choisi l'acide sulfurique. Afin d'étudier l'influence du pH sur le caractère général de la distillation, on dissout 25 g d'acide tellurique irradié dans un volume total (eau + acide) de 160 ml. On distille 10 fractions de 10 ml dont on ramène l'activité totale à une même valeur (1000 impulsions) et on peut ainsi comparer la vitesse de "libération" de l'activité sous forme d'iode.

Les résultats obtenus sont groupés dans le Tableau 1 et l'examen des activités totales distillées permet de constater qu'il existe une acidité correspondant à une relaxation plus rapide de l'iode: elle correspond au rapport 25 g H_6TeO_6/150 ml H_2O/10 ml H_2SO_4.

TABLEAU 1

Fractions	‰ d'activité totale distillée en fonction du volume de H_2SO_4 (pour 160 ml de solution)				
(10 ml)	0 (ml)	5 (ml)	10 (ml)	15 (ml)	20 (ml)
1	26	348	494	399	461
2	36	538	656	563	606
3	49	667	742	663	689
4	52	766	800	734	747
5	59	831	847	784	794
6	70	879	882	827	837
7	84	915	914	870	875
8	116	949	949	915	915
9	180	979	982	960	954
10	1000	1000	1000	1000	1000

Le flux intégré auquel a été soumis l'échantillon ne paraît pas fortement influencer les valeurs obtenues; en effet, on a opéré sur des échantillons ayant subit des flux intégrés compris entre $1{\cdot}08 \times 10^{15}$ et $2{\cdot}59 \times 10^{18}$ neutrons/cm^2 sans constater de modification de la vitesse d'entraînement de l'^{131}I.

Acidité des distillats

Etant donné qu'il n'a jamais été possible de mettre le tellure en évidence dans les distillats, on peut en déduire que l'acidité ne peut provenir que d'un entraînement de l'acide minéral utilisé. Cette constatation a amené à étudier l'entraînement de cet acide en fonction des quantités mises en oeuvre. Les résultats obtenus sont groupés dans le Tableau 2 qui donne les quantités d'acide qui furent déterminées dans des conditions standards de distillation. Les titrations furent effectuées potentiométriquement à l'aide de NaOH N/100.

Rendement de la distillation

Afin de vérifier la quantité d'iode-131 qu'il est possible d'extraire, on a effectué un essai sur 12·5 g d'acide tellurique ayant subi une irradiation totale de $2{\cdot}5 \times 10^{17}$

TABLEAU 2.—ACIDITÉ DES DISTILLATS EN FONCTION DES QUANTITÉS D'ACIDE MISES EN OEUVRE

Nombre de ml ajoutés à la solution de H_6TeO_6		Acidité des distillats (en ml NaOH N/100 pour 100 ml)
(*a*)	H_2SO_4	
	3·5	0·5
	5	2·9
	10	1·9
	15	4·8
(*b*)	H_3PO_4	
	5	2·7

Les résultats montrent
(a) Qu'il est important de ne pas utiliser d'excès inutile d'acide sous peine d'augmenter l'acidité des distillats.
(b) Que l'acide phosphorique n'est pas nettement supérieur à l'acide sulfurique du point de vue que nous préoccupe.
(c) Que les valeurs obtenues sont très satisfaisantes.

neutrons/cm². L'échantillon a été dissous dans 75 ml H_2O et 5 ml H_2SO_4 concentré et on a opéré comme suit:

- distillation de 50 ml dont on mesure l'activité spécifique,
- réajouter 50 ml d'eau au résidu de distillation et distiller à nouveau 50 ml dont on mesure l'activité,
- recommencer cette opération trois fois de façon à obtenir cinq distillats,
- ajouter au résidu: —45 ml H_2O
  —20 g $H_2C_2O_4.2H_2O$
- distiller 50 ml dont on mesure l'activité.

Après ce traitement, un contrôle par spectrographie γ montre que le résidu de distillation ne contient pratiquement plus d'iode. Les résultats de l'opération sont groupés dans le Tableau 3.

Le Tableau 3 montre que deux distillations sont suffisantes pour recueillir plus de 90% de l'iode formé. Il n'y a donc pas intérêt à distiller à nouveau, ni à effecteur une réduction par l'acide oxalique.

TABLEAU 3

Distillation	Activ. spécif. du distillat (μc/ml)	Activ. tot. receuillie (μc)	% de l'act. tot. recueil. au cours de la distillation	% de ^{131}I tot. recueil. au cours des distillations
1	136·0	6800	65·1	65·1
2	58·0	2900	27·8	92·9
3	9·2	460	4·4	97·3
4	3·2	160	1·5	98·8
5	1·3	65	0·6	99·4
Réduction par $H_2C_2O_4$				
6	1·1	55	0·5	99·9

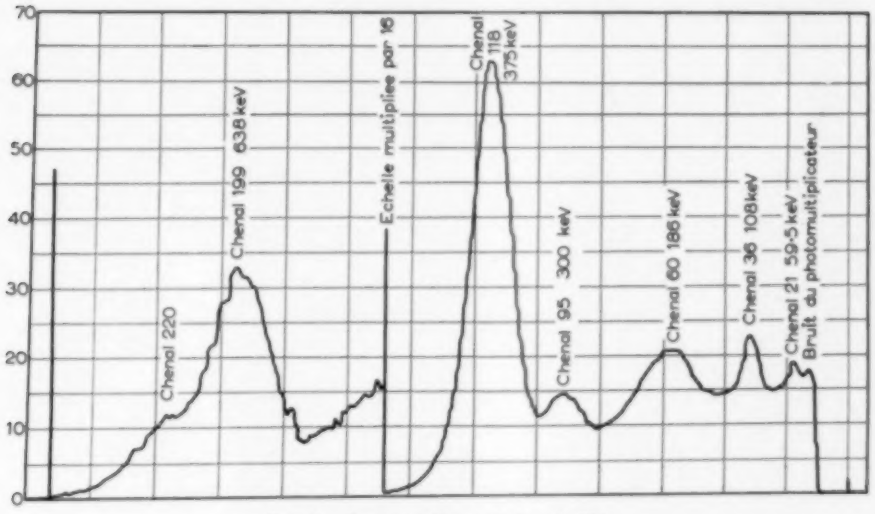

FIG. 1.—Spectre γ d'une solution de ^{131}I.

Etats valenciels de l'iode dans le distillat

On ne doit attendre que les seules formes distillables de l'iode, c'est-à-dire, I° et I^-. Dès lors, une extraction au tétrachlorure de carbone nous permettra une séparation et un contrôle des "formes actives". Pour ce faire, on irradie 25 g d'acide tellurique et on opère comme précédemment dans l'appareillage de distillation (150 ml H_2O/10 ml H_2SO_4).

On recueille 100 ml dans un jaugé contenant 1 ml d'une solution, environ N/10 en iode qui contient environ 20 g de KI par litre qui nous donne les quantités de "porteurs" nécessaires.

Le distillat est transféré dans une ampoule à décanter et agité avec 20 ml de CCl_4. Cette première extraction est suivie de deux autres de 10 ml. L'activité spécifique de cet extrait peut être soit mesurée directement dans un scintillateur creux du type Well, soit au compteur Geiger–Müller après extraction de la solution de CCl_4 par une solution de $Na_2S_2O_3$ et évaporation d'une aliquote.

La solution extraite est comptée dans des conditions identiques après dilution appropriée. Les résultats obtenus sont groupés dans le Tableau 4.

Ces résultats montrent l'indépendance totale qui existe entre le temps d'irradiation et l'état valenciel de l'iode distillé.

TECHNIQUE

Appareillage et méthode de production

L'appareillage (voir Fig. 2) est constitué d'un ballon *A* d'une capacité de deux litres, équipé d'un rodage sphérique 50/70 (*R*) et d'un réfrigérant à spirale relié par l'intermédiaire du siphon *S* à l'ampoule *B*. Il est chauffé à l'aide de la Jaquette *K* et est relié au ballon *C* d'une capacité de 1 l. par l'intermédiaire d'un dôme et d'un réfrigérant. Le tube *D* permet de le mettre en communication avec l'ampoule à siphonner *E*, munie d'un ajustage *V*, qui permet de mettre *E* en dépression. *C* est

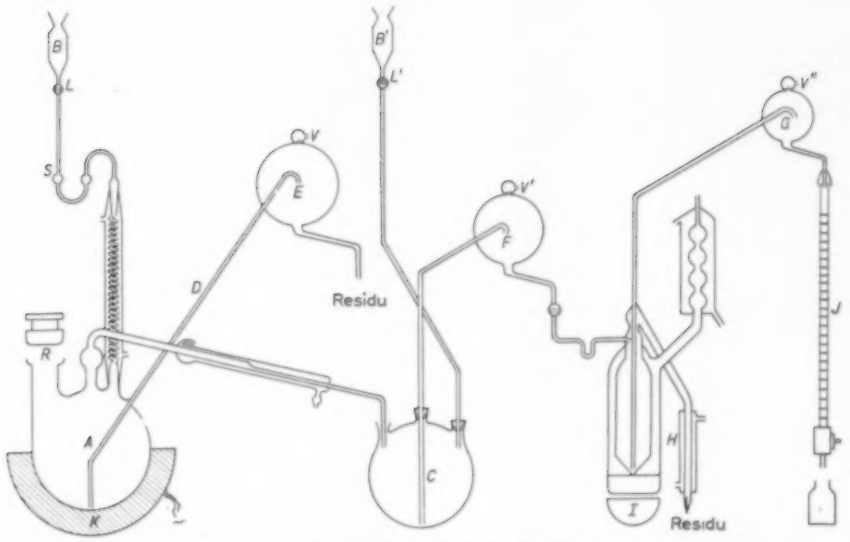

FIG 2.—Appareillage de production.

relié d'une façon similaire à l'ampoule *F* qui permet le transfert des liquides de *C* en *H* par application d'une dépression en *V'*. *H* est un évaporateur chauffé par l'épiradiateur *I* qui permet d'amener la solution au volume voulu après transfert par l'intermédiaire de *G* dans la burette *J*.

L'appareil de ce type qui est utilisé pour la production courante est enfermé dans une enceinte blindée à l'aide de briques de plomb de 6 cm d'épaisseur. Le contrôle à distance est simple. L'enceinte est maintenue en dépression pendant toute la durée de la préparation.

TABLEAU 4.—ACTIVITÉ DES DISTILLATS (1ère DISTILLATION) D'UN BATCH DE 25 g D'ACIDE TELLURIQUE IRRADIÉS DANS BR 1

Flux intégré (neutrons/cm²)	% d'activité dûe à I°	% d'activité dûe à HI	utilisé type de comptuer
$8{\cdot}1 \times 10^{11}$	44	56	G.M.
$2{\cdot}2 \times 10^{12}$	43	57	G.M.
$2{\cdot}2 \times 10^{12}$	44	56	Well
$3{\cdot}2 \times 10^{17}$	44	56	Well
$3{\cdot}2 \times 10^{17}$	43	57	Well
$1{\cdot}9 \times 10^{18}$	46	54	Well
$1{\cdot}9 \times 10^{18}$	44	56	Well

Etant donné les essais décrits précédemment, on opère finalement comme suit: on introduit 150 g d'acide tellurique "Analar," préalablement irradié, dans le ballon *A* (par le rodage *R*) qui contient une solution de H_2SO_4 (900 ml H_2O + H_2SO_4 concentré). Cette solution a évidemment été versée par l'intermédiaire de l'ampoule *B*. On ferme *R*. On introduit alors par l'ampoule *B'*, 15 ml d'une solution réductrice

$M/100$ en $Na_2S_2O_3$ et $M/50$ en Na_2CO_3 et $NaHCO_3$. On chauffe A (aprés s'être assuré de la fermeture des robinets L et L') et on distille 600 ml de solution. Cette solution est siphonnée en H, tandis que l'on ajoute 300 ml d'eau en A et 5 ml de solution réductrice en C. On distille à nouveau 200 ml. Le nouveau distillat est siphonné en H. On peut éventuellement recommencer une dernière distillation. L'évaporation est poursuivie en H jusqu'à un volume dépendant de l'activité spécifique désirée. La solution finale est transférée en J par simple application d'une dépression en V'.

Caractéristiques des solutions

pH : 7–9

matières solides : <3 mg/ml

Pureté: (a) le spectre γ ne permet pas de déceler d'émetteurs gammas autres que l'iode (voir figure),

(b) les courbes de décroissance effectuées au compteur G.M. et portant sur deux fabrications types ont permis de tracer des diagrammes qui ne nous ont pas permis de mettre en évidence l'existence d'éventuelles impuretés.

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RADIOCHEMICAL PROCEDURE FOR BERYLLIUM

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Abstract—A radiochemical procedure is given for the determination of beryllium activity in the presence of mixed fission products and uranium. Decontamination is achieved by adsorption of contaminants on anion-exchange resin from HCl solution, by ferric hydroxide scavenging, and by extraction of beryllium acetylacetonate from a weakly acidic EDTA solution. Two cycles of the procedure have results in a decontamination factor of 3×10^8 and a chemical yield of 90 per cent.

COSMIC-RAY-PRODUCED beryllium activity has been found in samples of rain,[1,2] snow[3] and air.[4] In such samples the beryllium activity must be radiochemically purified from nuclear bomb debris, primarily fission products. The procedure described here is a relatively simple and effective means of achieving this purification.

The procedure consists of three decontamination steps:

(a) Passage of an approximately 9 M HCl solution of the beryllium through a short anion-exchange column of Dowex-1 resin.
(b) Precipitation of ferric hydroxide from a strongly basic solution (beryllium is amphoteric).
(c) Extraction of beryllium acetylacetonate into benzene from a weakly acidic solution containing the sodium salt of ethylenediaminetetraacetic acid (EDTA)[5]

After completion of the decontamination steps, the beryllium is precipitated as the hydroxide, ignited to the oxide, transferred to a filter-paper disc, weighed to determine the chemical yield, and finally mounted for counting.

The extraction, step (c), is nearly specific for beryllium, but uranium, if present, will be nearly completely extracted. This has recently been made the basis of an analytical method for the determination of uranium.[6] This step was developed after several unsuccessful attempts at extracting basic beryllium acetate into chloroform.[7]

The ferric hydroxide precipitation, step (b), is a good general scavenger. Uranium is only partially removed in this step. Incomplete carrying is probably due to carbonate, which complexes uranium, in the sodium hydroxide reagent.

In step (a), uranium and many fission products are effectively removed by adsorption on the anion-exchange resin.[8]

To determine the degree of decontamination possible with this procedure,

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duplicate analyses were performed on a week-old fission-product solution which contained no beryllium activity. A known amount of beryllium carrier was added to a 9 M HCl solution of the fission products which contained 1·2 g of uranium. The uranium was removed by adsorption on a Dowex-1 anion-exchange column, then the procedure described below was followed (steps 2–10 twice). The chemical yield was 90 per cent and a decontamination factor (ratio of total counts/min added to counts/min in purified Be sample) of 3×10^8 was achieved. The residual counting rate in the sample was 3–4 counts/min of long-lived beta activity which was unidentified. This degree of decontamination and chemical yield have been confirmed by additional tests since the scheme was first developed in early 1953.

If analysis for tracer amounts of uranium or thorium is to be performed from the solution to which beryllium carrier is added, purification of the beryllium carrier may be necessary. Commercially available beryllium nitrate has been found to contain appreciable amounts of uranium and thorium activity. These can be readily removed by passing a 6 M HCl solution of beryllium through a Dowex-1 anion-exchange column to remove uranium, then through a Dowex-50 cation-exchange column to remove thorium. Alternatively, a mixed-bed column might be used.

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BERYLLIUM PROCEDURE

The detailed procedure is as follows:

1. Add beryllium carrier (15 mg of Be as the nitrate or chloride in dilute acid solution) to the solution to be analysed in a 40 ml centrifuge tube. Stir well, then precipitate $Be(OH)_2$ with a slight excess of NH_4OH. Centrifuge and discard the supernate.

2. Dissolve the $Be(OH)_2$ in 10 ml of conc. HCl. Pass this solution through a short anion-exchange column of Dowex 1X-10 resin which has been washed with HCl. (The short anion-exchange column is made by sealing a tip, 5 mm long $\times$ 2 mm dia., on the bottom of a 15 $\times$ 85 mm Pyrex test tube; plugging the tip with glass wool, and filling with resin to a height of about 2·5 cm.) Wash the resin with 5 ml of conc. HCl. Collect the effluent and wash in a 40 ml centrifuge tube.

3. Reprecipitate $Be(OH)_2$ with a slight excess of NH_4OH. Centrifuge and discard the supernate. Wash the $Be(OH_2)$ with 15 ml of water and discard the wash.

4. Dissolve the $Be(OH)_2$ in a minimum of HCl. Add 3 mg of Fe(III) carrier, dilute to 15 ml, and heat in a water bath. Add 10 ml of 8 N NaOH with stirring and heat until the $Fe(OH)_3$ precipitate coagulates. Centrifuge and decant the supernate into a 40 ml centrifuge tube.

5. Acidify the solution with HCl, then precipitate $Be(OH)_2$ with a slight excess of NH_4OH. Centrifuge and discard the supernate.

6. Dissolve the precipitate in 3 ml of glacial acetic acid and dilute to 15 ml. Add 2 ml of 10% EDTA solution, then adjust to pH 5 with NH_4OH. (Check pH with indicator paper.)

7. Add 2 ml of acetylacetone (2,4-pentanedione) and stir vigorously for a minute with a mechanical stirrer. Add 7 ml of benzene and extract the beryllium acetylacetonate by stirring vigorously for a minute using a mechanical stirrer. Allow the two phases to separate and transfer the benzene phase to a 40 ml centrifuge tube using a transfer pipette. Check the pH of the aqueous phase with indicator paper and readjust to pH 5 if necessary.

8. Repeat step 7 twice more, combining the benzene fractions in a 40 ml centrifuge tube. Discard the aqueous phase.

9. Back-extract the beryllium by adding 10 ml of 6 N HCl to the benzene solution and stirring vigorously for a minute. Allow the phases to separate and transfer the HCl solution to a 150 ml beaker, using a transfer pipette.

10. Repeat step 9 once. Combine the HCl fractions in the 150 ml beaker. Discard the benzene fraction.

11. Evaporate the HCl solution just to dryness (*do not bake*). Add 5 ml of conc. HNO_3 and evaporate *just to dryness*.

If a higher degree of decontamination is needed, dissolve the residue in 10 ml of HCl and repeat steps 2–10, starting with sentence 2 in step 2. Otherwise proceed with step 12.

12. Dissolve the residue from step 11 in 2 ml of conc. HNO_3 and 10 ml of water. Add a slight excess of NH_4OH to precipitate $Be(OH)_2$. Filter on to a Whatman No. 42 filter, using vacuum to speed the filtration. Transfer the paper and precipitate to a crucible and dry the paper under a heat lamp or in an oven at about 100°C. Ignite to BeO at 1000°C for an hour or until the precipitate is snow-white.

13. With the crucible inside a hood (to prevent inhalation of toxic BeO dust), grind the BeO to a powder with stirring rod. Transfer the oxide to a tared filter-paper disk by slurrying with ethanol. Wash with ethanol, dry at 90–100°C for 10 min, and weigh. The weighing should be done as rapidly as possible since BeO is somewhat hygroscopic.

14. Mount the BeO for counting. At this laboratory, the sample is mounted by sandwiching between two sheets of Pliofilm (ca. 0·6 mg/cm²) and securing to a brass disk (15/16 in. dia. × 1/4 in. thick) with an aluminium retaining ring.

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LETTERS TO THE EDITORS

Preliminary study on the kinetics of isothermal annealing of radiation damage in Szilard–Chalmers reaction with α-tris glycine cobalt (III)

(*Received* 26 *July* 1957)

THE annealing of the damage in neutron-irradiated compounds as a result of subsequent heating has been observed by several workers.[1–9] The present investigations are a part of a comprehensive study of thermal annealing in cobalt complexes which has been undertaken in this laboratory.

The annealing in tris-glycine cobalt (III) is found to be characterized by three or more first-order rate processes. The results on a sample stored at about 4–5°C for several months show that the thermal history is profoundly reflected in the annealing behaviour.

Experimental

The complex was prepared after LEY and WINKLER[10] and the α-form separated from its less soluble β-isomer by fractional crystallization.

The irradiation of the powdered sample of the complex was done in the thermal column of BEPO, Harwell, at "nvt" $\sim 1{\cdot}2 \times 10^{15}$ n/cm² and total γ-flux $\sim 2{\cdot}2 \times 10^{6} R$ at about 25°C.

Isothermal annealing runs were carried out as described by NATH *et al.*[9] The bulk and the aliquots were stored at 4–5°C to minimize annealing during storage.

Active cobalt species exchangeable with cobalt sulphate were extracted with chloroform as oxinate by a procedure similar to that followed by GENTRY *et al.*[11] and HILLIARD *et al.*[12] The aqueous and chloroform fractions were both made up to the same volume with the respective solvents, their activities measured in a scintillation counter assembly and the percentage retention calculated as before.[9] The data are given in Table 1. A saturation value of retention (R) was observed for all the runs. The plots of log $(R_\infty - R)$ vs. time t indicate that annealing is governed by three or more first-order rate processes as shown by A and A'' in the figure (corresponding to run 3 at 124°C in Table 1) which is representative of the various runs at different temperatures. The curve A represents the overall annealing resulting through superimposition of more than one first-order process. The curve A'', which represents the mixture of the faster processes, has been obtained by extrapolation of the linear rear portion (slow reaction) of the main curve A to the log $(R_\infty - R)$ axis and then subtracting its contribution from the main curve. The rear portion of curve A'' is again linear while the fore one is not, indicating that it could be further analysed (if the data had permitted) to give the fast and the not so fast processes. A'' is represented on a larger scale for the sake of clarity. The plot of log k vs. $1/T$ for the slowest annealing process gives the activation energy $\approx$ 13 kcal/mole in the temperature range studied. The numerical value of R_∞ as well as the magnitude of the anneal $(R_\infty - R_0)$ appear to be a function of the temperature of the run (refer to table) and the previous thermal history. The complex tagged with ^{60}Co, which was heated for 90 hr at 140°C, showed a decomposition of less than 0·2 per cent, indicating that the decrease of R_∞ at higher temperature cannot be accounted for by a first-order competitive thermal degradation of the complex.

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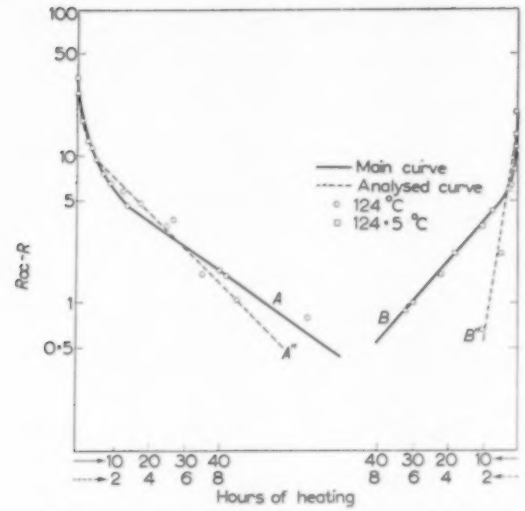

FIG. 1. *A*—run at 124°C which is indicated as No. 3 in Table 1.
B—run at 124.5°C on a sample stored for more than a year after the run *A*.
A'' and *B''* represent the graphically analysed curves and are shown on a different scale (of hours) for convenience.

TABLE 1

No. of the run	Temperature (°C)	Initial retention	R_∞ (saturation value for retention)	$(R_\infty - R_0)$	$(t_{\frac{1}{2}})$ half-time of the "reaction"	"k" in hr^{-1}	Frequency factor, Z from $\left(\ln k = \ln Z - \frac{E}{RT}\right)$
1	94·5	23·5	61·3	37·8	65 hr	0·01066	$2·046 \times 10^9$
2	110	26·0	64·5	38·5	33 hr	0·02100	$1·965 \times 10^9$
3	124	26·0	60·8	34·8	18·5 hr	0·03839	$1·965 \times 10^9$
4	131	30·0	60·0	30·0	15·0 hr	0·04619	1.782×10^9
5	140	27·0	57·5	30·5	9·0 hr	0·0770	$2·084 \times 10^9$
6	117	44·2	65·7	21·5	13·5 hr	0·05134	$3·530 \times 10^9$
7	124·5	47·2	67·4	20·2	11·5 hr	0·06026	$3·029 \times 10^9$

Runs 1–5 extended over a period of 5 months, run 6 was made 4 months later, and run 7, 6 months later still.

The effect of storage (equivalent to annealing at a lower temperature) is reflected as an increase in k in contra-distinction to the behaviour of tris-acetylacetone cobalt (III)[9] (refer curves *B*, *B''* corresponding to run 7 in Table 1 at 124·5°C on a sample stored for more than a year). This aspect as well as others are under detailed investigation with a freshly irradiated sample and the results will be published elsewhere.

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Kinetics of the isotopic exchange in the system CO_2—O_2 with ^{18}O as a tracer in a transparent quartz vessel

(*Received* 8 *April* 1958)

THE reaction of the exchange between CO_2 and O_2 has been measured at about 820–850–900°C. There is no measurable exchange between either of the thoroughly dried gases and the silica vessel at 900°C if the vessel is first baked out for several hours at 1000°C.

The exchange reaction was performed in a 30 mm diameter cylindrical transparent quartz vessel with a volume of 92 ml. Oxygen of 0·79 atomic per cent ^{18}O was used in these experiments. The reaction vessel was placed in a resistance-heated furnace. The furnace temperature was maintained constant to ±5°C, with a temperature gradient along the reaction vessel of less than 10°C. The samples were analysed by a 180° mass spectrometer.[1]

The rate of isotopic equilibration is given by a formula which corresponds with the expression for first order kinetics.[2]

$$S = -2{\cdot}303 \frac{P_{CO_2} \cdot P_{O_2}}{(P_{CO_2} + P_{O_2})t} \log (1 - x/x_\infty) \qquad (1)$$

wherein t = exchange time. The quantity x/x_∞ indicating the fraction of exchange is related to the ^{18}O concentrations as follows: $x/x_\infty = (^{18}Ot - {}^{18}Ot_0)/(^{18}Ot_\infty - {}^{18}Ot_0)$, where $^{18}Ot_0$ is the isotopic concentration of oxygen in CO_2 at zero time, ^{18}Ot the concentration after the measured exchange time t and $^{18}Ot_\infty$ the concentration in the equilibrium state. The value $^{18}Ot_\infty$ is calculated from the total ^{18}O concentration at the beginning of the experiment assuming that at t_∞ there is a proportional distribution of the ^{18}O atoms between the carbon dioxide and oxygen. (We neglect a possible isotope effect because the error due to this effect is small in comparison with the error in x/x_∞.)

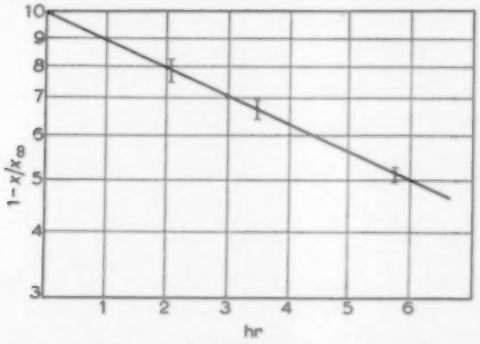

FIG. 1.—A semilogarithmic plot of $1 - x/x_\infty$ vs. time at 900°C
$P_{CO_2} = 54{\cdot}3$ mm Hg. $P_{O_2} = 44$ mm Hg.

The precision of the S-values is in general limited by the spread in the mass spectrometric ^{18}O determinations. This amounts to 1 per cent. It is evident from a series development of $\log (1 - x/x_\infty)$ that the inaccuracy in S is about the same as in x/x_∞. Because our measurements introduce a small difference in the numerator of (1) it appears that the inaccuracies in mass spectrometry give rise to a rather great error in S. This error varies from 10–25 per cent. To get an idea of the rate of exchange three experiments were made with a mixture at constant temperature (Fig. 1.).

The vertical lines associated with the experimental points represent an estimate of the error in the slope of the curve due to the error in x/x_∞.

The relation between the rate of the reaction (S) and the rate constant (k) is expressed by the empirical rate law:

$$S = k P^m_{CO_2} \cdot P^n_{O_2} \qquad (2)$$

[1] A. J. H. BOERBOOM, Thesis, Leiden (1957).
[2] H. A. C. MCKAY, *Nature, Lond.* **142,** 997 (1938).

k, m and n are calculated from equation (2) by measuring S for three independent mixing ratios CO_2/O_2 at one temperature.

TABLE 1.—DATA FOR CO_2/O_2 EXCHANGE EXPERIMENTS

T (°C)	k $\times 10^6$	m coeff. CO_2	n coeff. O_2
900	2·37	0·78	1·21
850	0·87	0·76	1·08
820	0·33	0·65	1·10

In testing the heterogeneous wall reaction the vessel was packed full of short sections of crushed quartz giving an increase in the surface to volume ratio of 17 times. The error of this value is of the order of 20 per cent.*

TABLE 2.—RATE CONSTANTS FOR PACKED (k_p) AND UNPACKED (k_u) VESSEL

T (°C)	k_u $\times 10^6$	k_p $\times 10^8$	Ratio k_u/k_p
900	2·37	4·3	1·8
850	0·87	5·8	6·7
820	0·33	4·6	13·9

When the ratios of k-values from Table 2 are compared, we immediately see that the rate of the heterogeneous reaction decreases with increasing temperature. At 820°C the ratio k_u/k_p is approximately equal to the increase in surface to volume ratio within experimental error, suggesting that up to this temperature the reaction is predominantly heterogeneous. At higher temperatures the decrease in the ratio indicates the increasing importance of the homogeneous reaction.

A detailed account of work in progress will be published in the near future.

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* This determination has been done at the Centraal Laboratorium van de Staatsmijnen te Geleen.

The chloride ion catalysed solvolysis of boron trichloride in liquid sulphur dioxide†

(*Received* 10 *April* 1958)

THE reaction $2BCl_3 + 3SO_2 \rightarrow 3SOCl_2 + B_2O_3$ was indicated by HECHT *et al.*,[1] who observed the first signs of reaction after five years at room temperature and tentatively identified the products after ten years. Recent thermochemical data[2] indicate that $\Delta H^\circ = -24$ kcal for the liquid phase reaction; and ΔF° also should be favourable.

† Abstracted from the Master of Science thesis by ERNEST R. BIRNBAUM, University of Southern California Libraries, 1958 (available on microfilm).

[1] H. HECHT, R. GREESE and G. JANDER, *Z. anorg. Chem.* **269**, 265 (1952).
[2] *National Bureau of Standards.* Circular No. 500 (1952).

We now find that this reaction is strongly catalysed by either sodium chloride or potassium chloride. For example, 1·303 g (11·1 mmole) of boron trichloride and 1·995 g (31·2 mmole) of sulphur dioxide, in a well dried bomb tube with 299 mg of vacuum-baked potassium chloride, changed to a plastic mass during two days at room temperature and after seven days seemed to be all solid. The volatile components were partially separated by high-vacuum fractional condensation. Each fraction was analysed by hydrolysis and titration for boron, chloride, strong acid, and sulphur (IV): (Found: 2·64 mmole BCl_3, 11·4 mmole $SOCl_2$, and 18·4 mmole SO_2). Thus 95·5 per cent of the sulphur was recovered in volatile form; and qualitative tests failed to disclose any sulphide, sulphite, or sulphate in the nonvolatile white solid.

This solid was investigated (with the aid of Mr. K. I. HARDCASTLE) by X-rays, giving a pattern which included lines characteristic of potassium chloride and boron oxide. It contained 8·55 mmole of boron (total recovery, 100·8 per cent) and 6·02 mmole of chloride—implying 2·01 mmole of chloride assignable to B–Cl bonds. The corresponding strong acid titration gave 1·83 mmole. This excess chloride (beyond the KCl) would represent an incomplete disproportionation of BOCl units, which could exist as mutually isolated components in the boron oxide polymer.

When ionic chlorides were absent, control experiments showed no reaction between sulphur dioxide and boron trichloride within a reasonable time.

The catalytic effect of chloride can be understood in terms of formation of a SO_2Cl^- ion,* which may well be a sufficiently strong base to bond to boron trichloride through oxygen. Loss of chloride from boron in the resulting complex, $ClS\overset{O}{\overset{\|}{O}}BCl_2^-$, would be a reasonable expectation; and a displacement of the $OBCl_2^-$ unit from sulphur by chloride also is possible. Thus one would have $SOCl_2$ and $KOBCl_2$, and the dissociation of the latter into KCl and the disproportionation products of BOCl would be expected.

This research began with an attempt to determine whether the hypothetical BCl_4^- ion is present sufficiently in the NaCl–BCl_3 solution in liquid sulphur dioxide[4] for transference of boron to the anode during electrolysis. The conductance was fairly high, but the solvolysis reaction prevented a decision concerning the transference. In any case, the specific ion BCl_4^- need not have been present, in view of alternative explanations of the solubility of sodium chloride in the presence of boron trichloride.

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* Presumably far less stable than SO_2F^-.[3]

[3] F. SEEL and H. JONAS, *Angew. Chem.* **67**, 32 (1955).
[4] D. M. GARDNER, Thesis, University of Pennsylvania (1955).

The back-extraction of uranyl nitrate from tributyl phosphate solution

THE optimum conditions for extraction of uranyl nitrate from nitric acid solutions by TBP were investigated in a preceding paper.[1] Back-extraction studies were made with a separated organic phase of 19 % TBP in kerosene containing uranyl nitrate extracted at 20°C from 5 g/l. aqueous uranyl nitrate containing 6 M HNO_3. Backwashing was carried out in similar manner to that of the extraction, 50 ml portions of the organic phase and of the backwashing solution being put into 100 ml stoppered conical flasks and shaken for 10 min in a thermostat at 20°C. The uranium content of the backwash phase was then determined and the percentage back-extracted calculated from $(x_2/x_1) \times 100$, where x_1 is the uranium concentration of the original organic phase and x_2 that of the backwash phase.

Sulphuric, hydrochloric, acetic and oxalic acids and their ammonium and sodium salts, and additionally ammonium and sodium carbonate, were chosen as back-extraction agents; 1, 5 and 10 w/w per cent solutions were employed, and the results compared with those from water backwash. The effect of backwashing with water alone was examined with varying volumes and also successive

[1] T. SATO, *J. Inorg. Nucl. Chem.* **6**, 334 (1958).

extractions with equal volumes. Uranium was determined gravimetrically, as in the previous paper.[1]

The results (Tables 1 and 2) show the effects of water, and of the acids and ammonium and sodium salts. Because of the low solubility of ammonium and sodium oxalates their effects at the higher concentrations could not be determined. Water as back-extraction agent is less effective than the other agents tested, except chlorides. However, successive equal volume backwashes with water gave 97 per cent back-extraction with two and 100 per cent with three treatments, whereas a single treatment with a three fold volume of water gave only 85 per cent back-extraction (Table 1). Since

TABLE 1.—BACK-EXTRACTION WITH WATER

		Water/solvent/volume		
		1	2	3
Single backwash	UO_2^{2+} backwashed (%)	43	68	85
Successive 1-volume backwashes	UO_2^{2+} backwashed (%)	43	97	100
	HNO_3 backwashed (%)	92	100	

part of the nitric acid is extracted into the organic phase during the initial extraction of uranyl nitrate,[2,3] it also will extract into the backwash solution.[4] The back-extraction of nitric acid during successive backwashes with water was examined, and it was found (Table 1) that the greater part of the nitric acid is removed in the first backwash together with about 40 per cent of the uranium, the

TABLE 2.—EFFECT OF THE ANIONS ON BACK-EXTRACTION WITH THE PARTICULAR CATIONS

Back-extraction agent	Percentage back-extracted		
	I*	II*	III*
$(NH_4)_2CO_3$	52·8	100	100
Na_2CO_3	56·7	100	100
H_2SO_4	60·2	68·5	79·4
$(NH_4)_2SO_4$	66·6	91·1	99·0
Na_2SO_4	62·0	87·6	96·7
HCl	42·8	35·4	24·2
NH_4Cl	51·4	39·6	34·4
NaCl	52·0	41·2	33·8
CH_3COOH	45·0	58·6	62·7
CH_3COONH_4	51·4	87·6	100
CH_3COONa	49·5	80·6	97·6
$(COOH)_2$	84·7	100	100
$(COONH_4)_2$	95·3	95·6	—
$(COONa)_2$	88·5	—	—

* I, II and III represent concentrations of 1, 5 and 10 w/w per cent respectively.

[2] R. L. MOORE, *AECD*-3196 (1951).
[3] K. ALCOCK, S. S. GRIMLEY, T. V. HEALY, J. KENNEDY and H. A. C. MCKAY, *Trans. Faraday Soc.* **52**, 39 (1956).
[4] E. K. HYDE, *Proceedings of the International Conference on Peaceful Uses of Atomic Energy, Geneva*, 1955, Vol. 7, p. 281. United Nations (1956).

bulk of the remaining uranium extracting into the second backwash. Presumably the $UO_2(NO_3)_2 \cdot 2TBP$ complex[2] is stronger than that of $HNO_3 \cdot TBP$[2,3] and consequently the preponderance of HNO_3 in the first backwash retards the back-extraction of uranyl nitrate. The strong complexing of uranyl nitrate by TBP may also account for the observation in the previous paper[1] that less nitric acid extracted into the organic phase in presence of uranyl nitrate than in its absence.

With the various agents examined, the results show (Table 2) that the effectiveness of back extraction decreases in the order oxalate > carbonate > sulphate > acetate, and that chloride retards the back-extraction. The ammonium salts of the acids are more effective than the sodium salts, both being more effective than the acids themselves. The effectiveness of the cations for back extraction of the uranium is dependent on their greater complexing affinity for uranyl *vis-à-vis* the $UO_2(NO_3)_2 \cdot 2TBP$ complex in the organic phase. The decreased back extraction by chlorides must be the result of the stronger complexing of uranyl chloride by TBP opposing the back extraction of uranyl ion as nitrate from the organic phase. It is seen, however (Table 2), that at 1 per cent concentration ammonium chloride and sodium chloride give slightly increased rather than decreased back extraction, whereas 1 per cent hydrochloric acid gives decreased extraction (as compared with water). Very probably at this low chloride concentration its complexing effect is too small to exert appreciable influence in the case of the salts, but with the 1 per cent acid itself the lowering of pH must be the important factor. The same tendency is evident with the other agents, the effects of the acids being inferior to those of their salts.

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The reaction between hydrogen peroxide and ruthenium tetroxide in acid solutions*

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THE net reaction between an excess of hydrogen peroxide and ruthenium tetroxide in perchloric acid solutions is the production of ruthenium(IV).[1] However, the course of the reaction is not simple and it has several interesting features which form part of the basis for this letter. Some experiments were also conducted with sulphuric acid as a reaction medium. These experiments showed that the anion must play an important role in determining the kinetics of the reaction as well as the intermediates which appear. Moreover, in sulphuric acid the net reaction between an excess of hydrogen peroxide and ruthenium tetroxide appears to be ruthenium(III).

EXPERIMENTAL PROCEDURE

Perchloric acid solutions were prepared by the proper dilution of Baker and Adamson's Reagent Grade perchloric acid. Acid titres were determined by standard analytical methods. Hydrogen peroxide solutions were prepared by the proper dilution of Merck's Reagent Grade 30 per cent hydrogen peroxide without stabilizer. Hydrogen peroxide normalities were determined by titration with a standard potassium permanganate solution. Solutions of about the desired concentration of ruthenium tetroxide were prepared according to the method of WEHNER and HINDMAN.[2] The concentration was determined by measuring the extinction of the solutions at 385 mμ and using the molar extinction coefficient, 930,[3] to fix the concentration. All absorption spectra were measured

* Presented at the Northwest Regional Meeting of the American Chemical Society, Pullman, Washington, June, 1953.

[1] L. W. NIEDRACH and A. D. TEVEBAUGH, *J. Amer. Chem. Soc.* **73**, 2835 (1951).
[2] P. WEHNER and J. C. HINDMAN, *J. Amer. Chem. Soc.* **72**, 3911 (1950).
[3] R. E. CONNICK and C. R. HURLEY *J. Amer. Chem. Soc.* **74**, 5012 (1952).

with a Cary Recording Spectrophotometer, Series 8, obtainable from the Applied Physics Corporation of Pasadena, California. The spectra were measured at room temperature. Quartz absorption cells were used for all samples.

Experiments were conducted by mixing a known ruthenium tetroxide solution and a known perchloric acid–hydrogen peroxide solution and following the reaction spectrophotometrically.

Sulphuric acid solutions were prepared and standardized in the usual manner. All other procedures were the same as used in the perchloric acid experiments.

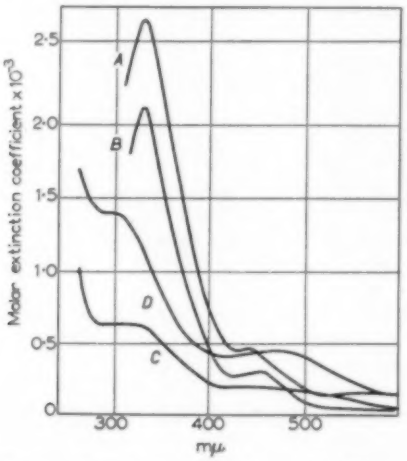

FIG. 1.—Spectra of species formed in the course of the reaction between hydrogen peroxide and ruthenium tetroxide in perchloric acid.
Initial conditions: 2 M H_2O_2, $5{\cdot}9 \times 10^{-4}$ M RuO_4, 1·1 M $HClO_4$.
Spectra of the solutions after mixing of the reactants: Curve *A*—3 min, curve *B*—2 hr, curve *C*—4 days, curve *D*—17 days.

Perchloric acid solutions

In perchloric acid the reaction between 1–2 M H_2O_2 and 10^{-4}–10^{-3} M RuO_4 is characterized initially by a very vigorous gas evolution which quickly subsides leaving the solution coloured yellow. The ruthenium tetroxide spectrum was not detected in solutions examined within 3 min after mixing. The yellow colour of the solution gradually fades and the brown colour characteristic of ruthenium(IV) slowly appears. During this time bubbles of gas from the decomposition of hydrogen peroxide are evolved. In solutions around 0·01 M ruthenium tetroxide or much more concentrated in ruthenium than that used in our experiments, and of the same hydrogen peroxide concentration, 1–2 M, the yellow intermediate is not observed and the ruthenium tetroxide goes very quickly to brown ruthenium(IV).[1] The course of a typical reaction is shown by the spectra in Fig. 1. The yellow species with an absorption maximum at 335 mμ gradually disappears and the absorption spectrum of ruthenium(IV) appears with its shoulder at 300 mμ and a broad maximum at 480 mμ. The spectrum obtained at 4 days, curve *C* of Fig. 1, indicated that a species whose colour intensity was less than that of the final product had been formed as an intermediate.

Sulphuric acid solutions

In sulphuric acid the reaction between 0·04 M H_2O_2 and 10^{-3} M RuO_4 is characterized by the measurable rate of disappearance of the ruthenium tetroxide. In addition, the catalytic activity of the ruthenium in decomposing the hydrogen peroxide is considerably less than that of the ruthenium in the perchloric acid solutions. Obviously, the anion is important in determining the speed of the reduction of ruthenium tetroxide by hydrogen peroxide and also the catalytic decomposition of hydrogen peroxide by ruthenium tetroxide. The spectrum due to ruthenium tetroxide gradually disappears and the spectrum of a new species with an absorption maximum at 290 mμ appears. The results of a typical experiment are shown in Fig. 2. The solution containing the species characterized

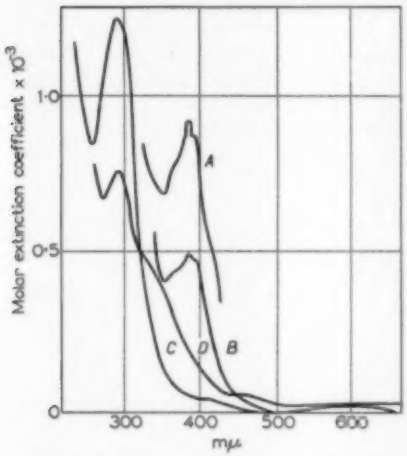

FIG. 2.—Spectra of species formed in the course of the reaction between hydrogen peroxide and ruthenium tetroxide in sulphuric acid. Excess hydrogen peroxide. Initial conditions: 0·0198 M H_2O_2, $8·8 \times 10^{-4}$ M RuO_4, 1·0 M H_2SO_4. Spectra of the solution after mixing of the reactants: Curve *A*—3 min, curve *B*—15 min, curve *C*—68 min, curve *D*—9 days.

by curve *D* of Fig. 2 did not give a positive starch–iodide test. This fact indicated that no hydrogen peroxide or ruthenium(IV) was present in solution. Moreover, this solution remained unchanged for over a month in a glass stoppered flask. The addition of chlorine water to the solution rapidly produced the brown colour characteristic of ruthenium(IV). It was, therefore, concluded that the ruthenium was present as ruthenium(III) and that the absorption maximum at 290 mμ was due to ruthenium(III)–sulphate species.

In Fig. 3 are recorded the spectra obtained from a sulphuric acid solution in which the hydrogen peroxide was not in large excess over the ruthenium tetroxide. In this solution the reaction proceeded

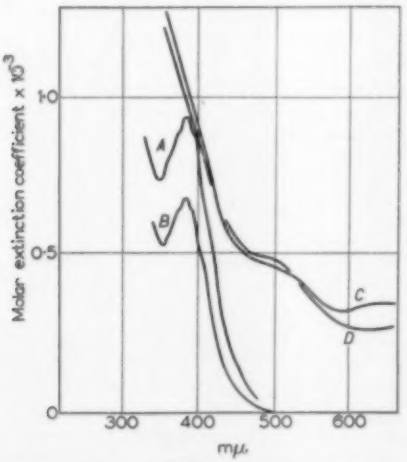

FIG. 3.—Spectra of species formed in the course of the reaction between hydrogen peroxide and ruthenium tetroxide in sulphuric acid. Insufficient hydrogen peroxide. Initial conditions: $24·9 \times 10^{-4}$ M H_2O_2, $11·0 \times 10^{-4}$ M RuO_4, 1·0 M H_2SO_4. Spectra of the solution after mixing of the reactants: Curve *A*—2 min, curve *B*—17 min, curve *C*—34 min, curve *D*—6 hr.

with the gradual disappearance of the ruthenium tetroxide apparently until the hydrogen peroxide was expended. At this point the excess ruthenium tetroxide reacted with the reduced ruthenium to give ruthenium whose absorption spectrum is represented by curve *C*. This solution was brown with a slight green colour. F. S. MARTIN[4] obtained similarly coloured solutions in which he demonstrated the presence of ruthenium(IV) and ruthenium(VI) sulphates. Thus, it seems likely that the solution represented by curve *C* was constituted in a like manner.

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[4] F. S. MARTIN, *J. Chem. Soc.* 3055 (1952).

The hydroboration of trimethylvinylsilane

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THE recent communication of WARTIK and PEARSON[1] which reports that the action of sodium borohydride in tetraethylene glycol dimethyl ether solution on vinyltrichlorosilane appears to cause cleavage of the vinyl–silicon bond, yielding monosilane as the ultimate product, prompts us to report some preliminary results of our investigations concerning the addition of boron hydride derivatives to vinyl–metal compounds.

When trimethylvinylsilane (0·375 mole) was added to a stirred solution of sodium borohydride (0·193 mole) and aluminium chloride (0·063 mole) in diethylene glycol dimethyl ether[2] and the resulting mixture was stirred at room temperature for 20 hr, a white precipitate resulted. Careful hydrolysis, either with dilute hydrochloric acid or with saturated ammonium chloride solution, was followed by separation of the organic phase and extraction of the aqueous layer with three 50 ml portions of diethyl ether. The combined organic layer was dried over $MgSO_4$. The solvents were removed by distillation and fractional distillation of the residue gave a 75 per cent yield of a triorganoborane, boiling over a range of 65–72° at 0·12 mm. (Found: C, 57·15; H, 12·66; B, 3·28. Calc. for $C_{15}H_{39}Si_3B$: C, 57·27; H, 12·50; B, 3·44%.) In a subsequent preparation the borane was not distilled, and the residue of essentially pure borane remaining after distillation of the solvent at reduced pressure was oxidized using the method of BROWN and RAO.[2] A mixture of organosilicon alcohols, b.p. 62–75° at 43 mm, was obtained. (Found: C, 50·83; H, 12·06. Calc. for $C_5H_{14}OSi$: C, 50·78; H, 11·93%.) Nuclear magnetic resonance studies[3] showed the mixture to consist of α-trimethylsilylethanol, $Me_3SiCHMeOH$, and β-trimethylsilylethanol, $Me_3SiCH_2CH_2OH$. A quantitative separation by fractional distillation could not be effected with the equipment available to us. In another experiment the crude undistilled alcohol mixture was analysed by vapour phase chromatography, and it was established that the β-alcohol and the α-alcohol were present in an approximately 2:1 molar ratio (63% β, 37% α). Comparison of the retention times of the alcohols in the mixture and of a sample of pure β-trimethylsilylethanol prepared by the method of SPEIER[4] served to establish that the first peak on the vapour phase chromatogram was due to the α-alcohol and the second to the β-isomer.

The reaction of trimethylvinylsilane (0·375 mole) with trimethylamine–borane, $Me_3N{\cdot}BH_3$, (0·102 mole) in diethylene glycol dimethyl ether solution at 80° gave an 85 per cent yield of organosilicon-substituted borane. The commercial availability of such amineboranes makes this synthesis of triorganoboranes from olefins preferable to that of BROWN and RAO, which is based on the enhanced reactivity of sodium borohydride in the presence of aluminium chloride. The amine–borane method of hydroboration is easier to carry out, less time-consuming, and the hydrolysis of the reaction

[1] T. WARTIK and R. K. PEARSON, *J. Inorg. Nucl. Chem.*, **5**, 250 (1958).
[2] H. C. BROWN and B. C. S. RAO, *J. Amer. Chem. Soc.* **78**, 5694 (1956).
[3] J. S. WAUGH, S. CASTELLANO and D. SEYFERTH, Report in preparation.
[4] J. L. SPEIER, J. A. WEBSTER and G. H. BARNES, *J. Amer. Chem. Soc.* **79**, 977 (1957).

mixture subsequent to the addition reaction is less vigorous than when the sodium borohydride–aluminium chloride reagent is used. In addition, yields of triorganoborane appear to be higher in the amine–borane reaction.

The organosilicon-substituted borane obtained by the latter method was oxidized to give β-trimethylsilylethanol and α-trimethylsilylethanol in exactly 2:1 molar ratio (66% β, 34% α). Thus in both reactions the borane (or the mixture of boranes) obtained has the approximate composition $(Me_3SiCH_2CH_2)_2BCH(CH_3)SiMe_3$.

These results show that the system under investigation presents an exception to the generalization made by BROWN and RAO[2] that terminal addition is always observed with the $NaBH_4$–$AlCl_3$ reagent, i.e.,

$$RCH{:}CH_2 + NaBH_4\text{–}AlCl_3 \rightarrow (RCH_2CH_2)_3B$$

Work in progress suggests that steric factors are of greatest importance in determining the structure of the triorganoborane obtained when a highly branched olefin such as trimethylvinylsilane reacts with trifunctional boron hydride derivatives. However, the main purpose of this communication is to point out that vinylsilicon cleavage by sodium borohydride does not occur when the three chlorine atoms in vinyltrichlorosilane are replaced by methyl groups. A complete report of this work and of work currently in progress will be given at a later date.

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VOL. 7 1958

Decay scheme of 2·1 hr ^{178}Ta *

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DURING the course of studies on the light tantalum isotopes, we have investigated the decay scheme of 2·1 hr ^{178}Ta. This isotope decays by electron capture (with a small positron branching)[1] to stable ^{178}Hf.

The ^{178}Ta was produced both by bombarding HfO_2 with 24 MeV deuterons and by bombarding Lu_2O_3 with 18 MeV α-particles. The former method yielded very intense samples of ^{178}Ta along with other light tantalum isotopes, whereas the latter method gave much weaker samples of ^{178}Ta of high isotopic purity. Chemical purification consisted of a combination of solvent extraction and resin-column techniques, and yielded carrier-free tantalum samples that were radioactively quite pure.

The electron lines of ^{178}Ta were studied using two 180° permanent-magnet electron spectrographs.[2] The lines were recorded photographically on Eastman no-screen X-ray plates. The effective magnetic fields of the two instruments were 99 and 216 gauss, and a resolution, $\Delta\rho/\rho$, of 0·1 per cent was obtained. Samples were prepared for electron analysis by electrodeposition of the tantalum onto a 0·010 in. diameter platinum wire. Six transitions were assigned to ^{178}Ta, having energies of 88·81, 93·17, 213·7, 325·8, 331·9, and 427·0 keV. These energies are expected to be accurate to within 0·1 per cent. Comparisons of the *L*-subshell ratios with the theoretical values of ROSE[3] indicate that the 93·17 and 213·7 keV transitions are E2. The *L*-subshell and *K*/*L* ratios for the other transitions were not determined well enough to make multipolarity assignments in this manner.

* Published for the U.S. Atomic Energy Commission.

[1] G. WILKINSON, *Phys. Rev.* **80**, 495 (1950).
[2] W. G. SMITH and J. M. HOLLANDER, *Phys. Rev.* **101**, 746 (1956).
[3] ROSE, GOERTZEL and SWIFT, privately circulated tables *Beta and Gamma Ray Spectroscopy* (edited by K. SIEGBAHN) Appendix IV. Interscience, New York (1955).

The γ-ray spectrum of ^{178}Ta was studied using a NaI(Tl) crystal coupled to a 50 channel pulse-height analyser. Coincidences between γ-rays could be measured by gating the 50-channel analyser with a selected region of the spectrum of a second NaI(Tl) crystal. Energy selection in the gating circuit was provided by a single-channel analyser. Samples for γ-ray analysis were prepared by evaporating to dryness small portions of the purified tantalum solutions onto 0·006 in. thick aluminum plates. *K* X-rays and photons of 90, 213, 330, and 426 keV were found in the γ-ray spectrum of ^{178}Ta, with relative intensities of 28, 17, 20, 27, and 18, respectively. Coincidence measurements showed that each of these γ-rays was in coincidence with all the others. In addition, consideration of the relative intensities of the peaks in the coincidence spectra revealed the following facts: (a) The intensity of the *K* X-rays in all the coincidence spectra was much less, relative to the other peaks, than in the singles γ-ray spectrum noted above. In some cases the *K* X-ray intensity was less than one-third that of one of the other peaks in the coincidence spectrum. (b) In the spectrum in coincidence with *K* X-rays the 330 keV peak was enhanced relative to the other peaks. (c) The 213, 330, and 427 keV peaks were of almost exactly the same intensity (after correction for counting efficiencies of the NaI crystal) in the spectrum in coincidence with 90 keV photons. Also, when any one of these three γ-rays was used as the gate, the intensities of the other two were the same within experimental error.

The absence of intense *K* X-rays from the coincidence spectra suggests that there is a delay occuring between the electron-capture event and the γ-ray emission. For this reason a search was made for the isomeric state in ^{178}Hf, and it was found to have a half-life of 4·8 sec.* The half-life measurement was made by chemically milking hafnium from the tantalum parent and following the decay on a single-channel differential pulse-height analyser connected through a count-rate meter to a Speedomax recorder. The 4·8 sec half-life was too short to make γ-ray or electron studies of the isomer convenient.

In constructing the decay scheme of ^{178}Ta it is essential to bear in mind that ^{178}Hf lies in a region of the periodic table where the "strong coupling" approximation of the unified nuclear model of BOHR and MOTTELSON[4,5] is good. Specifically, for an even-even nucleus the lowest-lying energy levels are expected to be given approximately by the formula

$$E = \frac{\hbar^2}{2\Im} I(I+1)$$

where E is the energy of the level, $\Im$ is the moment of inertia, and the spin, I, can take on values 0, 2, 4, 6, ... These levels should be connected by cascading E2 transitions. It would further be expected that the value of $\hbar^2/2\Im$ should be simialr to that of the neighbouring even-even nucleus, ^{180}Hf, or about 15 keV.[6]

The decay scheme shown in Fig. 1 may now be deduced in the following manner. The 330 keV peak seen in the γ-ray spectrum is expected to include both the 325·8 and the 331·9 keV transitions. From the fact that this peak is enhanced relative to the others when observed in coincidence with *K* X-rays, but drops in relative intensity when any other photons provide the gating pulse, it is concluded that one of these transitions precedes the isomeric state, and that the other one, along with the rest of the transitions, follows the delay. The selection of the 325·8 keV transition as the one that follows the delay is made because the energy of the peak coincident with the 213 or 426 keV photons was found to be 327 $\pm$ 2 keV. This is supported by the fact that the energy agreement with the rotational formula is considerably better than it would be for 331·9 keV. Of the five remaining transitions now thought to follow the isomeric state, four give excellent agreement with the rotational formula if assigned as shown in Fig. 1 (this agreement will be considered quantitatively below). To support this cascade arrangement are the facts that these transitions have all been shown to be in coincidence with one another, and that the intensities of the 213·7, 325·8, and 427·0 keV transitions have been shown to be very nearly equal. Also the 93·17 and 213·7 keV transitions have been shown to be E2 in agreement with the BOHR–MOTTELSON theory, and if the electron and γ-ray intensities are related by assuming the theoretical E2 conversion coefficients of the 213·7 keV transition, then the conversion coefficients of the 325·8, 331·9, and 427·0 keV transitions give the best agreement with E2 assignments

* We have learned in a private communication that COCHRAN, MIZE and BUNKER have also found this isomeric state.

[4] A. BOHR and B. R. MOTTELSON, *Phys. Rev.* **89**, 316 (1953); *Ibid.* **90**, 717 (1953); *Kgl. Danske Videnskab, Selskab Mat.-fys. Medd.* **27**, 16 (1953)
[5] A. BOHR, *Rotational States of Atomic Nuclei*. Ejnar Munksgaard, Copenhagen (1954).
[6] BURSON, BLAIR, KELLER and WEXLER, *Phys. Rev.* **83**, 62 (1951)

also. The relative intensities of the 325·8 and 331·9 keV photons in this case are deduced from the coincidence measurements.

The only choice remaining for the slow transition is the one of 88·81 keV. It can be shown that this γ-ray is very probably E1. Although the 88·81 and 93·17 keV photons cannot be resolved in the scintillation counter spectrum, an estimate of the intensity of the 93·17 keV photons can be made by assuming this transition has the same intensity as the other three rotational transitions. Correction of this intensity for conversion, using the theoretical E2 conversion coefficients of Rose,[3] gives the photon intensity. This relatively small contribution was then subtracted from the 90 keV peak, and the residual amount ascribed to 88·81 keV photons. Now, since the 88·81 keV transition feeds the

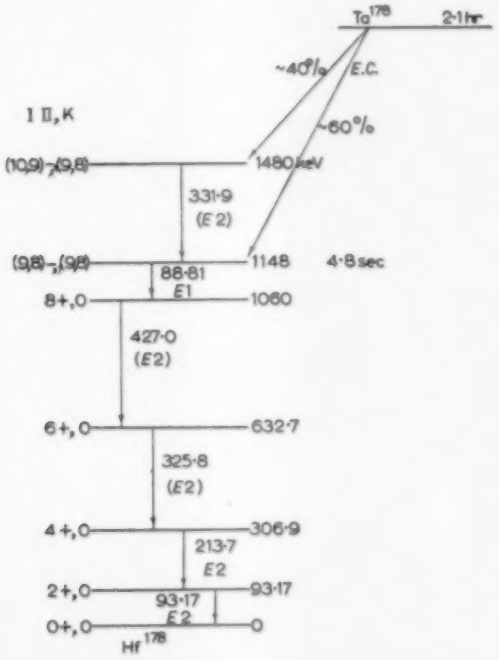

FIG. 1.—Decay scheme of ^{178}Ta. The approximate electron capture abundances were obtained from the relative photon intensities.

sequence of rotational levels, its intensity must be equal to or less than that of the individual rotational transitions. Thus, having a maximum transition intensity and a photon intensity, a maximum conversion coefficient of 0·5 may be calculated for the 88·81 keV transition, which allows only an E1 assignment. The similarity of the lower part of the decay scheme in Fig. 1 to that of 5·5 hr ^{180}Hf[6] is indeed remarkable.

Including a second-order correction term to the rotational equation given above, one obtains:

$$E = \frac{\hbar^2}{2\Im} I(I+1) - B[I(I+1)]^2,$$

where B (given explicitly in Bohr and Mottelson[4]) has to do with rotation-vibration interaction, but for these purposes can be considered a parameter to be empirically fixed. If the energies of the 2+ and 4+ states shown in Fig. 1 are used to fix $\hbar^2/2\Im$ and B, then they may be determined to be 15·61 and 0·013 keV respectively. Calculated energies for the 6+ and 8+ states are then 632·3 and 1056 keV, to be compared with experimental values of 632·7 and 1060 keV. The agreement is considered to be quite good.

Since the 4·8 sec isomer de-excites by an E1 transition to a level of spin 8+, possible spins of the isomeric state are 7, 8, and 9. The absence of decay to the 6+ state makes 7 seem unlikely. If the

331·9 keV γ-ray represents a transition between the first two levels of a rotational band based on the isomeric state, then $\hbar^2/2\mathfrak{I}$ for this band may be calculated to be 16·6 or 18·4 keV, depending on whether the base spin is chosen to be 9 or 8 respectively. Since $\hbar^2/2\mathfrak{I}$ for the ground state band is 15·6, a spin of 9 seems somewhat preferable to 8. The slowness of the 88·81 keV E1 transition may be understood in terms of the K quantum number, which represents the projection of the spin, I, on the nuclear symmetry axis. For the ground-state band K must be 0; however, for the 1148 keV state K is probably equal to the spin, either *8* or *9*. Thus while ΔI is only one for the 88·81 keV transition, ΔK is very likely 8 or 9, and in so far as K is a good quantum number E1 radiation is completely forbidden. The very long observed life-time indicates that K is, indeed, a rather good quantum number in this region of the periodic table.

Acknowledgement—We are indebted to Professor J. O. Rasmussen for many helpful discussions during the course of this work.

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NOTE

Alternations in electronegativity and the Pritchard and Skinner review

(*Received* 25 *March* 1958; *in revised form* 2 *June* 1958)

In 1955 Pritchard and Skinner[1] published a review on electronegativity in which they dismissed the "stability ratio" method of evaluation,[2] on fallacious grounds. Because it was believed that their error would be obvious to anyone examining the data to which they refer, a correction, unless volunteered by the review authors, seemed at first relatively unimportant. Unfortunately, however, there have been numerous evidences that readers of the review have accepted it as authoritative. Most recent is the very interesting paper by Allred and Rochow[3] on the electronegativities of the major group IV elements, in which the mistake of Pritchard and Skinner about stability ratios is again quoted. For this reason, it seems only fair to set the record straight, even though many who have read the review uncritically may not see this note.

Pritchard and Skinner objected especially to the report of alternations in electronegativity within a periodic major group. They stated: "... it seems to the authors of this review that the origin of the alternation in the stability ratio values lies in the alternation in the calculated electron densities of the inert gases..."

First, it should be noted that the authors quote these electronic density values from the first paper[4] and ignore the fact that in subsequent papers were used the revised values[2] of He 0·59, Ne 1·06, A 0·82, Kr 1·27 and Xe 1·41. (Incidentally, these values were not based on van der Waals or collision radii as implied by Allred and Rochow,[3] but on "nonpolar covalent" radii,[2] obtained by interpolation of crystal ionic radii of isoelectronic ions. For example, a value for Ne was obtained from the crystal ionic radii of $O^{=}$, F^{-}, Na^{+}, Mg^{++} and Al^{+++}.)

Table 1.—Electronic density and electronegativity variations[2]

	ED	ED_i	*SR*
B	2·16	0·76	2·84
Al	1·88	0·97	1·94
Ga	3·70	1·14	3·23
In	3·92	1·37	2·86
C	3·11	0·82	3·79
Si	2·46	0·94	2·62
Ge	4·20	1·17	3·59
Sn	4·28	1·38	3·10
N	3·95	0·88	4·49
P	3·04	0·91	3·34
As	4·67	1·19	3·91
Sb	4·68	1·39	3·37

[1] H. O. Pritchard and H. A. Skinner, *Chem. Rev.* **55**, 745 (1955).
[2] R. T. Sanderson, *J. chem. Educ.* **29**, 539 (1952).
[3] A. L. Allred and E. G. Rochow, *J. inorg. nucl. Chem.* **5**, 269 (1958).
[4] R. T. Sanderson, *Science* **114**, 670 (1951).

The major point to be made, however, is that inspection of the *ED* (average electronic density), ED_i (interpolated "ideal" or "inert" electronic density), and *SR* (stability ratio) values in question, reproduced in Table 1, shows that the most controversial alternations are originally present in the electronic density values of the active elements. Therefore the suggestion that they originate in values for the inert elements is without basis. Indeed, there is no alternation in the isoelectronic electronic density (inert) values, and in the transition from "inert-shell" to "18-shell" type element (period 3 to period 4), the increase is greater for electronic density than for stability ratio, showing that the effect of the inert values is actually to *diminish*, rather than cause, the alternations. Further, from argon to krypton and beyond, the trend of electronic density is steadily upward without alternation. Alternations in the groups of active elements in the periods 4, 5, and 6 therefore also cannot originate from inert element alternations.

The original observation of electronegativity alternations,[1] at least in group IV, has now received strong support in the work of ALLRED and ROCHOW,[2] and in other work referred to in their paper.

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[1] R. T. SANDERSON, *J. Amer. chem. Soc.* **74**, 4792 (1952).

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BOOK REVIEWS

K. W. BAGNALL: **Chemistry of the Rare Radioelements. Polonium–Actinium.** Butterworths Scientific Publications, London, 1957. x + 177 pp., 30s.

THIS is a useful and interesting book. Sponsored by The United Kingdom Atomic Energy Authority, Harwell, it has been written by an experienced worker in the field. The publication is opportune for two reasons: first because there is no other handy source of information about this collection of elements; secondly because two of them have recently become available in milligramme quantities, two others are relatively recent discoveries, and all have been the subject of research since 1940. Here are brought together a related sequence in the Periodic Table: polonium (84), astatine (85), radon (86), francium (87), radium (88) and actinium (89); respectively they are the heaviest members of the sulphur, fluorine, helium, lithium and scandium families. The common feature of the six elements is a dangerously high radioactivity and an inconveniently low availability. Though most text-books of inorganic chemistry deal, historically at least, with radium and radon they generally make scant or no mention of the others. It is desirable that the facts should be accessible for, as Dr. SPENCE says in his foreword, with "the development of atomic energy, elements which were previously unfamiliar to chemists have suddenly assumed technical importance".

Knowledge of the chemistry of polonium has advanced rapidly since it has been prepared in milligramme quantities by the neutron irradiation of bismuth. The author of this book has thereby been enabled to study the element itself and many of its compounds in visible and weighable amounts. His work makes it quite clear that the element falls properly into place as the fourth member of the sulphur sub-group. The resemblance it shows to tellurium is marked, such differences between them as do appear being all in the expected sense. Thus the element is more metallic than tellurium—indeed nearer to bismuth and thallium—and, though chemically somewhat more basic than its congener, has the dioxide, the di- and tetra-halides, and the compounds $PoSO_3$ and $PoSeO_3$ in proper character.

Astatine was identified in 1940, having been made by the α-bombardment of bismuth. The ^{211}At obtained—there are nineteen isotopes—was used for deducing its chemistry by trace procedure. It has a half-life of 7·23 hr and a specific activity of about 200 c/mg; thus a milligramme would produce so much heat and radiation as to render impossible the study of compounds by manipulating anything like this weight of the element. Solutions of about 10^{-13} molar strength have been used to observe its co-precipitation behaviour with iodine. The results leave no doubt that it is a halogen and that it differs from iodine in much the same way as iodine differs from bromine.

Radon has been recognized as an inert gas since the beginning of the century. Nevertheless it has continued to excite interest and no less than a third of the references to radon in this book bear dates from 1940 onwards.

Francium was discovered in 1939. It can be separated from the parent actinium by precipitating on suitable carriers first the actinium itself, then the radium and finally the thallium. The minute amounts thus obtained have provided evidence that it is an alkali metal with properties similar to those of rubidium.

Radium is the only one of these elements to be obtained in weighable amounts from natural sources. The classic work leading to its separation and identification as the fourth member of the calcium sub-group gave a remarkable impetus to the study of radioactivity. The element continues to be the subject of research.

Actinium, like polonium, has within the present decade been made in milligramme amounts, in this instance by the neutron irradiation of radium. Evidence from the trace chemistry has been extended and corrected by the preparation and study of weighable portions of the metal; the oxide, hydroxide and hydride; the halides and other compounds. The properties displayed are those associated with the rare earths.

The description of these elements is succinct and well documented; a few more dates in the text would have been useful, though these are there for the finding in the references. But Dr. BAGNALL

has done more than furnish current information on physical, chemical and radioactive properties, he has given a first-hand account of how the challenge of small quantities and dangerous radiation has been met in the laboratory. The section on the handling of polonium, illustrated by photographs including one in colour showing the metal as it appears in light from its own radiation, sets the tone of the treatment employed throughout. The experimental aspect is kept to the fore and where it calls for special treatment, as for instance with radium and actinium, this is given. Recognizing that the body of information about the individual elements varies greatly from one to another, the author has wisely allowed the space devoted to each to be governed by this consideration. The especially long section on polonium serves as a useful introduction to the rest of the text. Diagrams setting out the four radioactive decay series, a useful glossary of terms and abbreviations and an index are provided. The printing, paper and binding are good.

Although addressed to students and postgraduates, the book can also be recommended to the general reader curious about these matters and should certainly find a place in school libraries. It is of the stuff to fire the imagination of the bright young people wanted for science.

P. L. ROBINSON

Electromagnetically Enriched Isotopes and Mass Spectrometry. Edited by M. L. SMITH. Butterworths Scientific Publications, London, 1956. xvi + 272 pp., 45s.

THIS volume is an edited collection of thirty papers presented at a conference on *The Production and Utilization of Electromagnetically Enriched Isotopes* held at the Atomic Energy Research Establishment, Harwell, in September 1955. The conference was divided into seven sessions, each dealing with a particular aspect of the various fields included in the title of the meeting.

The papers of the first two sessions on ion source and collector problems are of somewhat restricted interest to the general chemist and deal with some of the main constructional problems of ion separators employing high source temperatures and high ion beam intensities. Particular attention is devoted to the ion source difficulties associated with the separation of low vapour-pressure elements, where thermal and chemical erosion of the source materials and electrical breakdown seriously reduce the working lifetime of the units. Cathodic sputtering would seem to offer a partial solution of the temperature problem. Consideration is also given to the sources for electromagnetic separation of radioelements. The collection of ion beams of high intensity causes considerable local heating and erosion with consequent evaporation and sputtering of the electrode material and collected isotopes, reducing the efficiency of separation and causing cross-contamination, which limits the purity of collected samples. Solutions of this problem and the methods used to retain gaseous or very volatile elements are described.

Beginning with a theoretical paper on the penetration of high energy ions into solids, the papers of the third session review the more chemical aspects of the choice and preparation of suitable compounds for use in ion separators, the chemical purification of the collected isotopes, and the preparation of targets for the study of nuclear reactions. Preferably, the elements themselves are used for isotope separation, but, for low vapour-pressure substances, the halides or oxides of the elements are generally used. Requirements of high chemical purity, freedom from moisture, and favourable mechanical properties (high density and large particle size) determine the methods of preparation. The very considerable difficulties encountered in the separation of the rare earth isotopes are described. The collected isotopes are always contaminated and chemical techniques akin to standard inorganic analytical methods are used for final refinement. The deposition of thin films of high purity isotopes on suitable substrates for studying nuclear reactions calls for methods giving deposits with high standards of chemical and mechanical suitability. In some cases, direct deposition in the ion separator is possible. But, in general, secondary methods external to the separator are preferable; of these, vacuum evaporation is the most versatile.

To anyone not acquainted with the application of stable isotopes to research, the scope might appear to be rather limited compared with the use of radioactive isotopes. The first two papers of the fourth session on the utilization of electromagnetically enriched isotopes serve to correct

this impression by indicating the very wide range of studies in which stable isotopes are of great practical value. The first paper surveys the stable isotope programme in the United States for the period 1946 to 1955, and the second describes the wide variety of investigations of nuclear properties carried out with isotopes separated at Harwell. The remaining papers of this session show in specific cases how stable isotopes are employed in nuclear reaction studies, spectroscopy, and solid state physics.

For both the production control of isotopes and some research problems using them, some form of mass analysis is necessary. The fifth session on isotopic abundance analysis deals with various aspects of this field, which is as important as the initial separation problem. The mass spectrometer offers by far the most versatile and comprehensive solution, though its use for low vapour-pressure elements presents ion source difficulties similar to those found for ion separators. In addition, there is the further complication of the necessity for the accurate quantitative comparison of different samples. A survey is given of the methods employed in the Oak Ridge and Harwell laboratories to surmount these and other difficulties. Isotope dilution analysis has proved to be a very successful analytical technique of comparative simplicity and high accuracy, especially useful for the estimation of trace elements. The theoretical and experimental aspects are well treated, illustrated by some instances of its application to research problems, of which the age determination of rocks provides an interesting example. A final paper in this session reviews some other methods (isotope shift of spectral lines, neutron absorption and radioactivation analysis) of mass analysis, none of which are of such wide application as mass spectrometry, but which offer definite advantages in specific cases.

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The papers of the last two sessions review the design of electromagnetic separators and the separation of radioactive isotopes. Like those of the first two sessions, they are of more interest to the specialist in the field, though some applications to research are given. Three papers on the Oak Ridge, Harwell and Scandinavian separators indicate the various approaches to separator design. A theoretical paper shows how the resolution of a separator can be increased using an alternating gradient magnetic field sector instead of the usual uniform fields, and some of the possibilities of the high frequency mass spectrometer are discussed. The two papers of the seventh session describe the separators used for radioelements and are illustrated by some research applications, including β-ray spectroscopy and fission studies.

A valuable addition to each paper is the inclusion of the ensuing discussion, adding some useful material and clarifying a few obscurities. The production of the book is good and the papers are amply illustrated with diagrams and photographs. As suggested before, the book is of limited interest to the general chemist, but will be of value to anyone using enriched stable isotopes or concerned with the construction of mass spectrometers. In the latter field, the book constitutes a valuable compilation of data on ion sources for the study of solids, for which the literature is rather incomplete.

W. J. DUNNING

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Papers to be published in future issues

C. H. SHIFLETT, M. E. STEIDLITZ, F. D. ROSEN and T. W. DAVIS, JR.: The chemical effect of alpha particles on uranium hexafluoride.

J. FAHLAND, G. HERRMAN und F. STRASSMAN: Zur Kinetik der elektrochemischen Abscheidung radioaktiver Ionernarten auf Metalloberflächen.

E.G. PROUT: The thermal decomposition of irradiated potassium permanganate.

D. C. WILLIAMS and S. KATCOFF: Branching in the decay of ^{97}Ru to ^{97m}Tc and ^{97}Tc.

D. C. WILLIAMS and S. KATCOFF: Neutron activation cross-sections of ^{96}Ru and ^{102}Ru.

F. J. JOHNSTON, D. A. HUTCHINSON and J. J. KATZ: Oxygen exchange between uranium oxides and water.

J. C. WALLMAN, P. GRAF and L. GODA: The specific activities and half-lives of americium-241 and americium-243.

D. F. PEPPARD, G. W. MASON, W. J. DRISCOLL and R. J. SIRONEN: Acidic esters of *ortho*phosphoric acid as selective extractants for metallic cations. Tracer studies.

C. J. HARDY, D. SCARGILL and J. M. FLETCHER: Studies on protactinium(V) in nitric acid solutions.

F. H. CRIPPS and J. W. WEALE: A new method for the absolute counting of ^{239}Np.

J. E. EDWARDS: Half-lives of ^{204}Ti and ^{134}Cs.

G. A. OLAH, A. E. PAVLATH and S. J. KUHN: Note on the preparation of iodine pentafluoride.

B. M. FOREMAN, JR. and G. T. SEABORG: Nuclear thermodynamics of the heaviest elements—II.

W. G. GEHMAN and W. C. FERNELIUS: The mechanism of racemization of the tris(ethylenediamine) cobalt(III) cation.

E. PUNGOR und J. TROMPLER: Beiträge zu den Eigenschaften des vierwertigen Chroms.

A. P. GINSBERG and J. M. MILLER: An empirical method for estimating the electron affinities of atoms.

W. M. OLSON and R. T. SANDERSON: The reaction of aluminium chloride with lithium borohydride.

R. C. YOUNG: Investigation of the black solid formed on reaction of uranium metal with hydrochloric acid.

A. A. WOOLF: The preparation of rhenium from iodo compounds.

T. V. HEALY and A. W. GARDNER: Correlation of absorption spectra and partition data for plutonyl nitrate in aqueous and organic media.

G. JANDER und G. WINKLER: Acetamid als nichtwässriges ionisierendes Lösungmittel—I. Konduktometrische Titrationen in geschmolzenem Acetamid.

G. JANDER und G. WINKLER: Acetamid als nichtwässriges ionisierendes Lösungmittel—II. EMK-Messungen und potentiometrische Titrationen in geschmolzenem Acetamid.

G. JANDER and G. WINKLER: Acetamid als nichtwässriges ionisierendes Lösungmittel—III. Lietfähigkeit und Stärke von Elektrolyten in geschmolzenem Acetamid.

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J. HALPERIN, J. O. OLIVER and H. S. POMERANCE: The thermal neutron absorption cross-section of ^{240}Pu.

F. A. COTTON and J. W. GEORGE: Properties of SF_4 and its adduct with BF_3.

F. M. BREWER, G. GARTON and D. M. L. GOODGAME: The preparation and crystal structure of gallium trifluoride.

A. J. ZIELEN, J. C. SULLIVAN and D. COHEN: The photochemical reduction and the autoreduction of neptunium(VI).

D. F. PEPPARD, J. R. FERRARO and G. W. MASON: Hydrogen bonding in organophosphoric acids.

G. R. CHOPPIN and S. G. THOMPSON: Electron capture half-life of ^{243}Cm.

NOBUYUKI TANAKA and TSUTOMU TAKAMURA: Spectrophotometric studies on thiocyanatocuprate(II) complexes in aqueous solution.

T. MOELLER, E. GOLGAS and R. H. MARSHALL: Observations on the rare earths—LXVIII. Partial resolution of yttrium and gadolinium acetylacetonates by means of a chromatographic technique.

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T. WARTIK and R. PEARSON: Reactions of carbon dioxide with sodium and lithium borohydrides.

S. ARONSON and J. C. CLAYTON: Kinetics of the reduction of U_3O_8 in hydrogen.

F. A. COTTON, H. STAMMREICH and G. WILKINSON: The Raman and infra-red spectra and structure of di(*π-cyclo*pentadienyliron) tetracarbonyl.

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P. REASBECK and J. E. WARREN: Radiochemical studies of the interaction of copper with 980 MeV protons.

S. M. ALI, F. M. BREWER, J. CHADWICK and G. GARTON: Co-ordination compounds of Ga(I)—I. Co-ordination compounds of gallous tetrachlorogallate and gallous tetrabromogallate with O- and N-donors.

L. J. REYNOLDS and G. WILKINSON: Some methyl*cyclo*pentadienyl–metal compounds.

K. W. R. JOHNSON: The preparation of high-purity plutonium metal.

R. F. BARNES, D. J. HENDERSON, A. L. HARKNESS and H. DIAMOND: The alpha and electron capture partial half-lives of ^{243}Am.

E. COLTON and L. ST. CYR: Some observations on phosphorus(III) *iso*cyanate.

C. H. BRUBAKER, JR. and C. E. JOHNSON: The effect of choice of solvent on the extraction of cobalt(III) thiocyanate complexes.

A. G. OSTROFF and R. T. SANDERSON: Thermal stability of some metal sulphates.

G. W. WATT and M. LUIS MUGA: The reduction of samarium(III) trifluoroacetate with potassium in liquid ammonia.

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A SELECTION OF ABSTRACTS AND TITLES OF PAPERS PRESENTED AT THE SECOND UNITED NATIONS INTERNATIONAL CONFERENCE ON THE PEACEFUL USES OF ATOMIC ENERGY

GENEVA, SEPTEMBER 1958

(Correct at time of going to Press)

P/7. Fission product yields from highly irradiated ^{239}Pu. E. A. C. CROUCH and I. G. SWAINBANK (United Kingdom).

1. The rare earth fission products have been isolated from the products of the irradiation of ^{239}Pu with a total dose of $2{\cdot}3 \times 10^{22}$ neutrons/cm^2 The rare-earths, after separations from the transuranic elements, were themselves separated on the micrograms scale by means of a micro cation-exchange column, and the isotopic composition and absolute quantity of each element determined by mass-spectrometry and micro-chelatometry, or by neutron activation analysis.
2. The isotopes estimated were ^{139}La, ^{140}Ce, ^{142}Ce, ^{144}Ce, ^{141}Pr, ^{142}Nd, ^{143}Nd, ^{144}Nd, ^{145}Nd, ^{146}Nd, ^{148}Nd, ^{150}Nd, ^{147}Sm, ^{148}Sm, ^{150}Sm, ^{151}Sm, ^{152}Sm, ^{154}Sm, ^{152}Eu, ^{153}Eu, ^{154}Eu, ^{155}Eu, ^{156}Gd, ^{158}Gd, ^{160}Gd. The isotopes ^{159}Tb, ^{160}Dy, ^{162}Dy, ^{163}Dy, ^{164}Dy, were also found to be present but were not estimated.

P/26. The actinide oxides. L. E. J. ROBERTS (United Kingdom).

1. This paper discusses some chemical properties of the actinide oxides and of solid solutions of these oxides with each other and with other oxides. The subjects chosen are relevant to the use of UO_2 and PuO_2 as reactor fuels, either as ceramics or in dispersed systems such as cermets and slurries.
2. Equilibrium pressures of oxygen over the UO_2–U_4O_9–U_3O_8 composition range are being directly determined at high temperatures. These results are used to calculate the oxygen pressures below which the cubic UO_2–U_4O_9 phases are stable at various temperatures. The rate of oxidation within this composition range can be approximately calculated from diffusion coefficients for interstitial oxygen determined at low temperatures. The process of phase division into the two cubic phases, UO_2 and U_4O_9, that occurs on temperature cycling is accompanied by particle division.
3. The cubic UO_2 structure can be stabilized at higher oxygen pressures by making solid solutions with other 4-valent oxides such as ThO_2 and ZrO_2; excess oxygen can be incorporated interstitially in all such structures. Equilibria between UO_2–ThO_2 solid solutions and oxygen have been measured over a wide range of pressures, temperature and composition. The degree of oxidation under given conditions diminishes as uranium content decreases, mainly because the heat of solution of oxygen in the lattice decreases.
4. Uranium dioxide forms a number of "anomalous" solid solutions with trivalent and divalent oxides and the stability of the fluorite structure is such that extensive solid solutions can be formed between UO_2 and oxides such as MgO and Al_2O_3, which do not dissolve appreciably in stoicheiometric UO_2, if sufficient oxygen is present to complete the MO_2 structure. The diffusion of oxygen through such structures containing U and anion vacancies seems anomalously rapid as compared to oxygen diffusion through ThO_2 containing anion vacancies.
5. From such studies, certain predictions can be made about the behaviour of solid solutions containing PuO_2 and NpO_2, which cannot be easily oxidized in the pure state. Some forms of PuO_2 can be oxidized as far as $PuO_{2\cdot1}$ but NpO_2 has not been oxidized beyond $NpO_{2\cdot01}$ despite the stability of Np_2O_5 at low temperatures. UO_2 and ThO_2 form solid solutions with NpO_2 and PuO_2; preliminary results on the preparation, stability and oxidation of these solid solutions are recorded, together with some data on "anomalous" solid solutions containing the transuranic elements.

P/113. Effects of gamma rays and neutrons on molecular and ionic crystals, as ascertained by pure quadripolar nuclear spectroscopy. JULES DUCHESNE (Belgium).

Work recently carried out in our laboratories (*C. R. Acad. Sci., Paris* **238**, 1801, 1954; *Physica*, **22**, 541, 1956) established that very low concentrations of a substance (an impurity) can be detected, in a solid solution, by the analysis of the quadripolar spectrum which characterizes the more abundant compound. A law of the form $I/I_e = e^{-r_r C}$ made it possible to relate the intenseness of the lines to the molecular concentration of the impurity. With several co-workers, (*J. Chem. Phys.* **23**, 1969, 1955; *C. R. Acad. Sci., Paris* **243**, 259, 1956), we were able to show that a relationship of the same type holds good when the impurities are caused to appear in the matter by radiations of various types (for instance the gamma rays produced by ^{60}Co, and neutrons). A simple method, which does not in any way affect the samples, but which is limited by the requirement that good quality spectra be obtained was immediately developed in order to arrive at some estimate of the relevant damage (chemical transformations and lattice defects). It was applied, in particular, to the determination of the resistance of some molecular and ionic crystals to radiation (aromatic and alicyclic halogenated derivatives; iodoform; sodium chlorate, etc.). The results obtained provided a base for discussion of the problem of the relationships between the molecular structure and radiation resistance, as well as a review of the questions related to the recovery phenomena and the oxygen effect.

P/137. The extraction of plutonium at various oxidation potentials. GÖRAN CARLESON (Sweden).

An investigation has been made of the extraction of plutonium in tracer amounts by 40 per cent tributyl phosphate (TBP), diluted in kerosene from nitric acid solutions of varying concentration, either pure or containing small amounts of some oxidizing or reducing agents. Distribution coefficients have been determined for Pu(III), Pu(IV) and Pu(VI) and their partition curves constructed.

P/138. Free radical reactions induced by fast neutrons, X-rays and gamma rays in different materials. L. EHRENBERG and G. AHNSTRÖM (Sweden).

The production of free radicals formed in living and dead materials as a consequence of irradiation was measured by means of electron spin resonance at 3 cm wavelength. The following radiations were used: 175 kV X-rays, 2 mm Al filtration; ^{60}Co γ-rays; and fast neutrons (unmoderated fission spectrum in the Stockholm reactor).

In a given substance different radiations give radicals of the same e.s.r. spectrum. Within the limits of error of dosimetry the radical yield per dose unit in glycine or sorbitol was independent of the kind of radiation. In teflon a similar correspondence was found, which is interesting, since, due to total absence of hydrogen, the neutron energy is dissipated via carbon and fluorine ions.

In order to get high and more accurately known dose-rates of dense ionizing radiations, irradiations of boron containing compounds by thermal neutrons was included in the investigation. $Na_2B_4O_7 \cdot 10H_2O$, B_2O_3, sorbitoldiboric acid and Pyrex-glass give fairly stable radicals, whereas the decay is rapid in decylboric acid.

In amorphous compounds—where atom-groups are mobile and/or diffusion of oxygen possible—a more rapid decay of radicals occurs than in crystalline solids or glasses. The influence of water-content and oxygen-tension on the decay of radicals in starch and living plant seeds has been studied.

P/140. A fast method for the determination of cobalt in steel for reactor construction by means of activation analysis. TORBJÖRN WESTERMARK, INGRID FINEMAN and KNUT LJUNGGREN (Sweden).

The method is based on the use of the metastable isomer ^{60m}Co which precedes the long-lived ^{60}Co after neutron capture. ^{60m}Co emits 59 keV gamma radiation and has only 10·8 minutes half-life. This enables the use of a very short activation time, about 10 minutes in the Stockholm reactor R1 at $5 \cdot 10^{11}$ /ncm² sec. The method has been applied to various Swedish steels. Here the presence of manganese is the most disturbing factor which has so far prevented the use of the direct spectrometric analytical technique (thick NaI-crystal scintillation detectors and a single channel pulse height analyser). A fast chemical procedure (especially developed by INGRID FINEMAN) has been used to avoid this difficulty. It involves rapid dissolving of steel turnings in hydrochloric acid, extraction of iron into diethylether and selective precipitation (after addition of carrier) of cobalt with nitroso-naphtol. The procedure also makes self-absorption of the soft gamma radiation negligible. A small activity of long-lived ^{60}Co is added to the dissolving acid. This is chosen so as not to disturb the spectrometry, but to enable correction for losses of cobalt during the procedure. The standard consists of a small filter paper on which a small volume of cobalt solution is evaporated. The whole procedure after activation takes 30–40 minutes and seems to be capable of achieving a sensitivity limit of 1–2 μg at the neutron flux used. The estimated maximum error is 5–10% in the region 50–150 p.p.m. if the sample is 0·1 g and the above mentioned flux is used.

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P/201. Mass-spectrometric studies of pile poisons and their yields in the fission of ^{233}U, ^{235}U and ^{239}Pu. D. R. BIDINOSTI, H. R. FICKEL and R. H. TOMLINSON (Canada).

A mass-spectrometric comparison of fission yields obtained at various neutron fluxes and irradiation times has made possible the measurement of pile-neutron absorption resulting from the accumulation of several fission products in a D_2O-moderated reactor. The following pile-neutron absorption cross-sections have been measured relative to $^{59}Co = 36{\cdot}0$ barns: $^{133}Cs = 40$ barns, $^{147}Pm = 207$ barns, $^{149}Sm = 85{,}000$ barns, $^{151}Sm = 11{,}500$ barns. Some of these values are considerably higher than thermal-neutron values because of resonance absorption.

P/203. Radiochemical methods applied to the determination of cross-sections of reactor interest. T. A. EASTWOOD, A. P. BAERG, C. B. BIGHAM, F. BROWN, M. J. CABELL, W. E. GRUMMITT, J. C. ROY, L. P. ROY and R. P. SCHUMAN (Canada).

The results (in barns) are as follows:

Neutron Capture Cross-Sections of Fission Products for Reactor Neutrons

^{85}Rb	$1{\cdot}0 \pm 0{\cdot}3$	^{133}Cs	$30{\cdot}0 \pm 1{\cdot}7$
^{89}Sr	$(5{\cdot}8 \pm 0{\cdot}4) \times 10^{-3}$	^{134}Cs	139 ± 12
^{90}Sr	$0{\cdot}42 \pm 0{\cdot}05$	^{135}Cs	$10{\cdot}6 \pm 0{\cdot}5$
^{91}Y	< 10	^{140}Ba	<20
^{129}I	27 ± 3	^{143}Pr	125 ± 14
^{130}I	18 ± 4		

Capture Cross-Sections of Heavy Nuclides

$^{236}U\ (n, \gamma)\ ^{237}U$: $\sigma_{2200} = 5{\cdot}5 \pm 0{\cdot}3$, resonance integral $= 257 \pm 22$

$^{233}Pa\ (n, \gamma)\ ^{234}Pa$ (1·18 m): $\sigma_{2200} = 27$ (tentative), resonance integral $= 193$ (tentative)

$^{233}Pa\ (n, \gamma)\ ^{234}Pa$ (6·7 hr): σ for reactor neutrons $= 28$ (tentative)

The neutron fission cross-sections have been measured by comparing the fission rate of ^{240}Pu, for example, chemically separated from its parent ^{244}Cm, with a standard in a "back-to-back" ionization chamber in a thermal-neutron beam in NRX. The results (in barns) are as follows:

^{238}Pu $16{\cdot}5 \pm 0{\cdot}4$ (resonance fission integral 40 ± 10)

^{239}Np $<1{\cdot}0$, ^{240}Pu $<0{\cdot}1$, ^{242}Pu $<0{\cdot}2$.

P/271. Synthetic inorganic ion exchangers and their applications in atomic energy. C. B. AMPHLETT and J. M. HUTCHEON (United Kingdom).

1. Highly stable, granular, selective ion exchangers are being studied with a view to their application to the treatment of high-temperature pressurized water, chemical separations in intense radiation fields, and for normal separations where increased specificity is desirable.

2. These materials include zirconium phosphate, arsenate, tungstate, molybdate, and oxide; oxides and phosphates of thorium and titanium, and, tungsten oxide. The salts possess cation-exchange properties; tungsten oxide is a cation-exchanger, whilst the other oxides are amphoteric and may be used for either cation or anion exchange depending on the conditions. In the case of zirconium phosphate, the effect of variation in manufacturing method on the properties of the product has been studied on the 1 kg scale using standard pilot-scale equipment, and several large batches have been prepared for comparative testing, over a range of mesh sizes suitable for large-scale column operation.

3. These materials buffer water and aqueous solutions to a pH dependent upon the parent material, the cation substituted in it, and the degree of substitution, and therefore offer promise of supplying water buffered to a steady pH by a simple means. The rate of exchange of ions is sufficiently rapid for them to be useful in removing ionic fission products and corrosion products from circulating systems. Static high-temperature tests in water at 300°C have shown that physical breakdown is not serious; there is no sudden production of fines, and the particle-size distribution curve moves slowly towards smaller particle sizes without altering in shape. An open-circuit column has been built to work at 300°C and corresponding pressures; this is being used to obtain breakthrough curves at high temperatures and to study physical and chemical breakdown in flow systems.

4. Column separations have been carried not with zirconium phosphate in the alkali metal and alkaline earth series, the specificity being greater than that using organic resins: other separations are being studied. Zirconium oxide is capable of separating groups of cations in acid and neutral solutions by virtue of differences in hydrolytic properties, e.g. although at pH 4 it is normally an anion exchanger and will not exchange cations such as Cs^+ or Sr^{2+}, hydrolysable ions such as Fe^{3+} and Cr^{3+} are readily taken up. Such separations could be of use in purifying radioactive Cs and Sr from polyvalent impurities, corrosion-products, etc., and separations of transition-metal ions among themselves should be possible.

5. The stability of these materials towards both α- and β-irradiation is very much greater than that of organic exchangers, indicating their usefulness in chemical processing in very intense radiation fields.

P/300. The reduction of uranium hexafluoride by carbon tetrachloride. D. A. COLLINS, J. S. NAIRN and J. C. TAYLOR (United Kingdom).

Uranium hexafluoride dissolves in carbon

tetrachloride at ordinary temperatures to form a reasonably stable solution. When heated to temperatures of 150°C and above, however, a rapid reaction takes place which is simply expressed as follows:

$$UF_6 + CCl_4 \rightarrow UF_4 + Cl_2 + \text{chlorofluoromethanes.}$$

Some excess CCl_4 is required to take the reaction to completion, and a molar proportion of $4CCl_4 : 1UF_6$ is satisfactory. Apart from the UF_4, the products of the reaction are volatile even at ordinary temperatures and can be removed in a stream of warm air. The UF_4 product is in a form suitable for direct reduction by calcium or magnesium to uranium metal of high quality suitable for fuel element fabrication.

P/304. The chemistry and metallurgy of neptunium. H. A. C. McKay, J. S. Nairn and M. B. Waldron (United Kingdom).

1. Gram quantities of neptunium have been isolated from process wastes, and have been employed in the following studies.

Dry chemistry (*D. A. Collins, J. A. S. Mowat, G. M. Phillips and M. H. Rand*).

2. NpO_2 and Np_3O_8 have been prepared by the ignition of precipitated Np(V) hydroxide, the former at high temperatures (600° or 1000°C) and the latter at lower temperatures (150° or 300°C) in air. Their stoicheiometry and crystal structure have been studied, as well as the decomposition of Np_3O_8 on heating. NpF_4 has been prepared by heating NpO_2 to 600°C in a stream of HF and O_2, and its structure confirmed. Reduction of NpF_4 with excess Ca in an argon atmosphere yielded Np metal in 98·7 per cent yield.

Solution chemistry (*D. A. Collins, E. Hesford, J. J. Hillary, H. A. C. McKay, K. W. Sykes and B. L. Taylor*).

3. The use of Fe(II) and of N_2H_4 to reduce neptunium to the IV-state in nitric acid solution, and of O_3 to oxidize it to the VI-state have been studied.

4. Electron transfer spectra due to Np(IV) complexes with nitrate, sulphate and chloride, and to Np(VI) complexes with nitrate and sulphate, have been observed in the ultra-violet. The threshold wavelengths fall in the order expected from the electron affinities and ionization potentials of the ions concerned. Correlations can be made with spectral changes at longer wavelengths, due to complexing. No such changes could be found in the Np(V) spectrum between 400 and 1000 mμ over a range of 1–8 M in nitrate ion.

5. The extraction of Np(IV) and Np(VI) from nitrate solutions by dibutyl carbitol and tributy phosphate has been investigated.

Neptunium metal (*G. C. Curis, V. W. Eldred, J. A. Lee, P. G. Mardon and J. A. C. Marples*).

6. Physical property measurements have been carried out on ca. 20 g. of neptunium metal. These demonstrated the existence of three allotropic modifications α, β and γ between 20°C and the melting point, 640 ± 50°C. Dilatometric measurements show the $\alpha - \beta$ and $\beta - \gamma$ transformations on heating as 273 ± 5°C and 577 ± 10°C respectively. X-ray examination confirms the structures for the α- and β-phases reported by Zachariasen. Thermal expansion measurements coupled with the measured density of the α-phase 20·2(5) g/cc (of theoretical X-ray value, 20·4(5)) suggest values 19·3(6) and 18·3(1) g/cc for the densities of the β- and γ-phases respectively.

The specific heat of the α-phase over the range 60–200°C varies between 0·03–0·04 cal/g°C which gives a value for the atomic heat in excess of the theoretical Dulong and Petit value.

The α-phase has a Vickers hardness number of 355; the Meyer index and number are 2·19 and 458 respectively.

P/446. Fused SnF_2 fuels for nuclear reactors. B. J. Thamer, G. E. Meadows, R. M. Douglass, B. M. Carmichael, M. E. Battat and R. P. Hammond (U.S.A.).

The salt SnF_2 is thermally stable. It has a melting point of 213°C and a boiling point of 850°C. Its wide liquid range and high boiling point should allow convenient operation without appreciable pressure at temperatures of reactor interest. The cross-section for neutron capture in tin is 0·6 barns for thermal neutrons and about 0·03 barns for 1 MeV neutrons. Neutrons capture in fluorine is nil. Hence SnF_2 is potentially feasible as a fuel solvent for either a thermal or a fast reactor.

Studies of the phase diagram of the system UF_4–SnF_2 have been made by the techniques of filtration, differential thermal analysis and quenching, with identification of the solid phases by means of chemical analysis, the polarizing microscope and X-ray diffraction. Three uranium-containing solid phases are observed, namely, UF_4 and the two previously unreported compounds $UF_4 \cdot SnF_2$ and $UF_4 \cdot 2SnF_2$. Each of the latter two compounds melts incongruently The eutectic composition and temperature are 0·5 mole per cent UF_4 and 212°C. The peritectic point at which the compound $UF_4 \cdot 2SnF_2$ melts is at 4·5 mole per cent UF_4 and 340°C. That for the compound $UF_4 \cdot SnF_2$ is at 7·8 mole per cent UF_4 and 371°C. Other solubilities are 1·0, 2·0 and 10·0 mole per cent UF_4 in SnF_2 at 250°, 285° and 420°C, respectively. Optical, X-ray and morphological data have been obtained for the two new compounds, $UF_4 \cdot SnF_2$ and $UF_4 \cdot 2SnF_2$, and for SnF_2.

Plutonium tetrafluoride is unstable in SnF_2, giving PuF_3 in its place. The solubility of PuF_3 in SnF_2 is 0·41, 0·52 and 0·63 mole per cent PuF_3 at 350°, 450° and 550°C, respectively. The solid phase is PuF_3(s). The solubility of the PuF_3 at 450°C is lowered to 0·22 mole per cent PuF_3 by the presence of 10 mole per cent UF_4.

P/535. The recovery of uranium from highly irradiated reactor fuel by a fused salt volatility process. G. I. CATHERS, W. H. CARR, R. B. LINDAUER, R. P. MILFORD and M. E. WHATLEY (U.S.A.).

A fused salt fluoride volatility process is being developed at Oak Ridge National Laboratory for recovering uranium from either molten fluoride salt fuel or zirconium–uranium heterogeneous reactor fuel. The basic step in the process is conversion of the uranium to UF_6 with F_2 in a fluoride salt melt—with volatilization of the UF_6 from the melt. In the case of the zirconium–uranium fuels the fuel element is dissolved in a fluoride salt melt with hydrogen fluoride at 600 to 700°C, while with the molten fluoride fuels the UF_4 is a constituent of the melt. Volatile fission product fluorides are removed from the UF_6 in an absorption-desorption step with a pair of NaF beds, and the decontaminated UF_6 is collected in cold traps. Compared to aqueous processing, the fused salt fluoride volatility process has fewer chemical steps in the overall uranium fuel cycle, an appreciably lower waste volume, and the probability of a more compact plant.

Two fluoride salt systems have been studied for use in the hydrofluorination dissolution step. The NaF–ZrF_4 system remains liquid at 600°C over the composition range of 40–60 to 60–40 mole per cent, while the LiF–NaF system, with a liquidus temperature 675°C at 57–43 mole per cent, can dissolve up to 55 mole per cent zirconium at 600°C. Dissolution rates in laboratory studies of zirconium coupons were satisfactory with both systems. The results of dissolution studies of portions of nonirradiated zirconium–uranium fuel elements are reported.

Volatilization of 99·8 per cent of the uranium from NaF–ZrF_4–4 mole per cent UF_4 at 600°C with a F_2/U mole ratio of 4 or 5 has been demonstrated.

Since decontamination of the volatile ruthenium and niobium fluorides is not appreciable in the fluorination step, a double bed NaF absorption-desorption step is required. The UF_6 and niobium are absorbed on the first bed at 100°C while a large part of the ruthenium passes through. When the UF_6 is desorbed with F_2 at 100–400°C essentially all the niobium remains on the first bed. The second NaF bed removes any activity carried from the first bed in the UF_6 stream.

The UF_6 is collected in two cold traps operated in series at −40 and −60°C, respectively, followed by a bed of NaF to absorb minute amounts of UF_6. The UF_6 is drained from the traps after heating and liquefaction.

Overall gross β- and γ-decontamination factors of 10^6 have been demonstrated in the Laboratory. Factors of $>10^7$ have been demonstrated for cesium, strontium, zirconium, and the rare earths. The process has been demonstrated in a laboratory facility capable of handling up to 10^4 Mwd/ton short cooled uranium.

A pilot plant capable of processing 50-litre batches of fused salt containing up to 10 kg of uranium was constructed and operated at ORNL. In a series of demonstration runs on nonirradiated uranium, 95 per cent of the uranium was accounted for with only 0·03 per cent lost in the waste salt from the fluorinator. The results of the runs made to recover the uranium from the Aircraft Reactor Experiment molten salt fluoride fuel are presented. Initial materials of construction for the pilot plant were L-Nickel for the fluorinator, Monel for UF_6 and F_2 lines and the fluorine disposal system, Inconel for the absorbers, and copper and Monel for the cold traps. An attempt is being made to obtain a more satisfactory material of construction for the fluorinator. Hydrofluorination equipment is being installed in the pilot plant to make possible the processing of zirconium-highly enriched uranium heterogeneous reactor fuel elements.

P/537. Americium and neptunium recovery processes. W. H. LEWIS, J. R. FLANARY, R. E. BROOKSBANK, R. E. LEUZE and R. D. BAYBARZ (U.S.A.).

Solvent extraction processes have been developed and demonstrated through a pilot plant scale for recovering neptunium-237 and americium-241 from irradiated uranium and fuel cycle wastes. Neptunium has been recovered from the following sources: (1) irradiated normal uranium, (2) irradiated enriched uranium and (3) fluorination ash produced from the conversion of recovered UO_3 to UF_6. Americium has been separated from a fuel cycle waste which contained large quantities of lanthanum and cerium. Final purification of neptunium and americium from solvent extraction processes was achieved by ion-exchange methods.

The Purex process, which uses 30 per cent tributyl phosphate as solvent and nitric acid as salting agent, is employed extensively for separating and decontaminating uranium and plutonium from irradiated natural uranium. With only minor modifications to an existing Purex flowsheet, neptunium was recovered as a purified product in addition to uranium and plutonium. Two cycles of solvent extraction were required for this separation. Separation of plutonium from uranium and neptunium was

accomplished in the first cycle. Neptunium and uranium were separated and recovered as purified products in the second cycle. Approximately 90 per cent of the neptunium in the feed solution was recovered as product. The neptunium was separated from uranium by a factor of 10^5 and contained only a trace of plutonium.

The process for recovering neptunium from irradiated enriched uranium was developed for use on aluminium-uranium alloy fuels. In this process the fuel was dissolved in nitric acid, and two cycles of solvent extraction, using tributyl phosphate for the extractant and aluminium nitrate as the salting agent, were required for separation and decontamination of uranium and neptunium. In the first cycle uranium and neptunium were recovered and decontaminated from fission products and impurities using 2 per cent tributyl phosphate for the extractant. Separation and further decontamination of uranium and neptunium were accomplished in a second solvent extraction cycle using 15 per cent tributyl phosphate. Product recovery exceeded 99 per cent for uranium and neptunium.

Another source of neptunium was the fluorination ash which was produced from the conversion of recovered UO_3 to UF_6. Recovery of the uranium and neptunium from this material was accomplished by using a process flowsheet which provides for dissolution, one solvent extraction cycle using 15 per cent tributyl phosphate as the solvent, and product concentration by evaporation. The ash was dissolved in boiling aluminium nitrate–nitric acid solution to provide a feed solution for solvent extraction. Aluminium was used as a fluoride complexing agent in order to increase the extractability of uranium and neptunium. Solvent extraction was accomplished in a battery of three contactors. In the first contactor, uranium and neptunium were extracted from the feed with 15 per cent tributyl phosphate and scrubbed with an aluminium nitrate–nitric acid solution to remove extracted impurities. The organic phase then flowed to a second contactor in which the neptunium was preferentially stripped from the solvent with 0·5 M HNO_3. In the third contactor, the uranium was stripped from the organic phase with 0·01 M HNO_3. In this process, approximately 99 per cent of the neptunium was recovered from the feed solution and the neptunium was separated from the uranium by a factor of 10^6.

A solvent extraction process for separating gram quantities of americium from kilogram quantities of lanthanum and cerium was developed and demonstrated through a pilot plant scale. The recovery process for americium required two solvent extraction cycles. In the first cycle americium, lanthanum and cerium were extracted from a neutral nitrate feed containing aluminium, iron, calcium and magnesium using tributyl phosphate. In the second cycle the americium was separated from the lanthanum and cerium by acidifying the product solution from the first cycle to 17 M HNO_3, and selectively extracting the americium with tributyl phosphate. Under these conditions, most of the lanthanum and cerium remained in the aqueous phase. In both cycles the americium was back-extracted from the tributyl phosphate with 4·0 M HNO_3, followed by product concentration by evaporation. Final purification was accomplished by selectively eluting americium from cation exchange resin with citrate solutions.

P/574. Crystal structure of U_3O_8 determined by neutron diffraction. A. F. ANDRESEN (Norway).

The capability of neutron diffraction in locating light atoms in the presence of heavy atoms has been utilized in the study of the crystal structures of some uranium oxides. For U_3O_8 the investigations lead to a structure somewhat different from that proposed by W. H. ZACHARIASEN on the basis of X-ray results. The structure is closely related to that of UO_3 but involves a relocation of some of the oxygen atoms and a slight displacement of some of the uranium atoms. The symmetry conforms with the orthorhombic group $C222$.

P/643. Radiochemical studies of the fast-neutron fission of ^{235}U and ^{238}U. L. R. BUNNEY, E. M. SCADDEN, J. O. ABRIAM and N. E. BALLOU (U.S.A.).

Radiochemical studies of the fast-neutron fission of ^{235}U and ^{238}U have been made in the mass region beyond mass 143 with two neutron energy distributions. These studies provide measurements of the relative fission yields of several chains in the rare earth group in fission of ^{235}U and ^{238}U caused by neutrons with an energy distribution very close to unmoderated fission neutrons and by neutrons with an energy distribution peaked at 8 MeV. The increased contribution of very asymmetric modes of fission as the energy of the compound nucleus is increased is clearly shown by the results. In the fission of ^{238}U the yield at mass 161 is increased 2·9 times at the higher neutron energy.

No previous measurements have been published on radiochemical studies of the fission of ^{238}U at these neutron energies beyond mass 144 except at mass 156 for the lower neutron energy.

P/690. An experimental study of fission in the actinide elements. A. SMITH, P. FIELDS, A. FRIEDMAN, S. COX and R. SJOBLOM (U.S.A.).

The results of a recent experimental investigation of the fission properties of some actinide elements are presented. The experimental study

includes the following topics: fission fragment kinetics, fission neutron spectra, prompt gamma-rays from fission, delayed neutrons from fission.

The kinematic distribution of the fission fragment modes of $^{229}Th + n_{th}$, ^{240}Pu,[1] $^{241}Pu + n_{th}$, ^{242}Pu,[1] ^{243}Cm,[1] ^{244}Cm,[1] ^{252}Cf,[1] and ^{254}Fm[1] were determined experimentally using a high resolution back-to-back ionization chamber. The results are presented in topological form. The experimental data were further analysed to give directly the primary fission fragment mass yield distributions and the total fission fragment kinetic energy distributions as a function of mass ratios. Empirical expressions relating the most probable total fragment kinetic energy to $Z^2/A^{1/3}$ and the most probable mass ratios to Z^2/A are proposed.[2] The relations are in good agreement with the results of this experiment and with characteristics of previously known fission processes.

The fission neutron spectra of $^{233}U + n_{th}$, $^{241}Pu + n_{th}$ and ^{252}Cf[1] have been measured from 0·2 to 10·0 MeV. Time of flight techniques were employed to determine the lower energy portions of the spectra and proton recoils in emulsions were used to study the higher energy neutrons. The measured spectra are well described by the empirical relation:

$$N[E(\text{MeV})] \alpha \sinh [cE(\text{MeV})]^{1/2} \exp [-bE(\text{MeV})]$$

where $N(E)$ is the number of neutrons of energy E per unit energy interval and b and c are constants characteristic of the particular fission process. If it is assumed that the highly excited primary fragments are well represented by the statistical nuclear model, then the fission neutron emission can be interpreted as a "boil off" and the nuclear temperature can be adjusted to give a good fit to the measured fission spectra. Intercomparison of the spectra measured here with the known spectra of ^{235}U and ^{239}Pu indicates that the mean fragment temperature and the average neutron energy are slowly increasing functions of Z^2/A.

The prompt (<10 mμsec) fission gamma-ray spectrum of ^{252}Cf[1] was measured from 0·075 to 10·0 MeV using single and double crystal scintillation spectrometers. The spectral distribution, consisting of ten gamma-rays with a total energy of 8·2 MeV per fission, is essentially a monotonically decreasing function of the gamma-ray energy. The total energy release per fission in the form of quanta is slightly larger than in the case of ^{235}U, and considerably greater than predicted by theory.

The periods and yields of the delayed neutron groups emitted in the fission of ^{252}Cf[1] have been measured. The integrated yield per fission was found to be —1/100 that of ^{235}U. The delayed neutrons are primarily associated with heavy fragment precursors. The light precursor groups found in the fission of ^{235}U, such as ^{87}Br are markedly absent. By correlating the significantly different mass and delay neutron yields of ^{252}Cf with those of the lighter fissile isotopes a self consistent scheme of delayed neutron precursors is obtained. This set of precursors is extended in to mass regions not amenable to more direct treatment.

This abstract presents the results of a programme at the Argonne National Laboratory extending over the past two years. It is hoped that these results will contribute substantially to the fuller understanding and utilization of the fission phenomena.

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[1] Indicates the fission process studied is spontaneous.
[2] Throughout this abstract Z and A refer to the charge and mass number of the fissioning nucleus.

P/825. Methods of production and uses of transplutonium isotopes. STANLEY G. THOMPSON (U.S.A.).

The methods and equipment used in the production of transplutonium isotopes during the past ten years will be described and discussed. The following subject matter will be included.

(1) Experimentally determined isotopic compositions resulting from long-term irradiations of ^{239}Pu in the Materials Testing Reactor are given. Calculated curves are shown for isotopic compositions at various neutron fluxes as a function of time not only for fluxes now available but also for fluxes at high as 5×10^{15}. Tables of neutron-capture and fission cross-sections are given.
(2) The methods and equipment used for chemical processing and purification of the products of neutron-irradiated material and for preparing material for irradiation are described.
(3) Techniques and methods are described for the preparation and handling of cyclotron targets. Methods used for rapid separations by chemical and recoil methods are described. Data are given concerning several types of procedures for preparing thin sources.
(4) A summary is given of the cross-sections for the production of transplutonium isotopes in bombardments with charged particles and very heavy ions.
(5) The uses of the heavy isotopes in basic research and some other possible applications are discussed.

P/914. Analysis for plutonium by controlled potential coulometry. F. A. SCOTT and R. M. PEEKEMA (U.S.A.).

A method for the determination of the plutonium content of reactor fuels has been developed using controlled potential coulometry. This method is superior to conventional procedures because it is independent of the plutonium isotopic content, has greater precision and sensitivity, and can be used for plant feeds and in-process solutions as well as the plutonium product.

The plutonium content of solutions has been determined over a wide concentration range with a precision of from ±0·1 per cent to ±1 per cent on samples containing from 2 to 0·05 mg, respectively. Either mercury or platinum electrodes are used, and the method is simple with a minimum of sample pretreatment and no chemical adjustment of valence state necessary. For most work, electrical calibration of the coulometer is sufficient, thus obviating the necessity of chemical standards. The plutonium (IV) to (III) valence change is reversible, and rapid checks on a sample may be obtained by a simple change in the controlled electrode potential. In the course of the work, the polarographic behaviour of Pu(IV) was studied in detail in many media.

Interferences have been studied, particularly of reactor fuel alloying elements and fission products, and tolerable levels of common interfering ions defined. The method has been applied to the determination of the plutonium content of metal pieces with a precision of ±0·1 per cent at the 95 per cent confidence level, and also to the direct estimation of the plutonium content of reactor fuel processing solutions.

P/930. The molecular properties of hydrogen fluoride. D. F. Smith (U.S.A.).

The vibrational and rotational constants of hydrogen fluoride have been evaluated from the frequencies of the lines of the rotation and vibration-rotation spectrum. The intensities of the lines of the fundamental vibration-rotation band, when used with the internuclear distance, 0·9171 Å, indicate that the dipole moment increases at the rate of 1·6 Debye units per ångstrom as the internuclear distance is increased. The permanent dipole moment, 1·736 Debye units, was determined from dielectric constant measurements at microwave frequencies.

In addition to these properties of isolated hydrogen fluoride molecules, the effects of intermolecular interactions are present in the spectrum and the dielectric constant behaviour. The line breadth and shape studies show that the line breadth for pure hydrogen fluoride is determined primarily by resonant dipole forces, but that with other gases other intermolecular force laws pertain. There is not only a variety of line breadths, but of line shapes as well. In addition, pressure induced line shifts for molecular lines have been observed for the first time. The line breadths can be used to compute molecular collision diameters. For example, the $R(0)$ line of hydrogen fluoride at 100°C shows a 6·74 Å collision diameter for a hydrogen fluoride–uranium hexafluoride collision.

These studies have important application in the development of a chemical analysis for hydrogen fluoride. In corrosive vapours containing hydrogen fluoride, the only satisfactory methods of analysis involve the infra-red spectrum. Because the apparent absorption with conventional spectrometers depends upon such a wide variety of parameters, the standard empirical calibration, using synthetic samples, results in a large and elaborate series of working curves if any variety of samples are encountered. A method of analysis, using the measurements from which the collision diameters have been determined, has been developed. This method avoids the need for the preparation of synthetic samples whenever the analysis conditions are changed. The method has been used, for example, to monitor the hydrogen fluoride concentration in a uranium hexafluoride gas stream where hydrogen fluoride concentrations of 0·1–1·0 mole per cent were determined to within ± 0·05 mole per cent.

In addition to the hydrogen fluoride vapour spectrum of monomer, the polymer spectrum has also been studied. It has been established that this polymer spectrum originates from dimeric, tetrameric, and hexameric hydrogen fluoride, with dimer and tetramer always minor constituents. From the dielectric constant studies, the 2nd virial coefficient of the monomer is found to be sizeable. When this is taken into account, the vapour density measurements can be reconciled with the present interpretation. The hexamer has a small dielectric constant and probably has a cyclic structure. In addition to the hydrogen fluoride polymers, the spectrum of vapour phase mixtures sometimes contains a band of a molecular complex such as ClF_3·HF, SO_2·HF, or CO_2·HF, present in very small concentration. On the other hand, large concentrations of complexes are found from the spectrum of mixtures of hydrogen fluoride with vapours of diethyl ether, acetone, and methanol.

In dilute liquid solutions, the spectrum of hydrogen fluoride contains bands of hydrogen fluoride polymer. In very dilute solutions the polymer spectrum is reduced in intensity. With some solvents, such as uranium hexafluoride and molybdenum hexafluoride, the absorption remaining corresponds to monomeric hydrogen fluoride. In other cases, as with bromine trifluoride, sulphur dioxide, and chlorine trifluoride the hydrogen fluoride absorption corresponds to a molecular complex which obscures the monomer absorption. The adjustment of the concentrations in a mixed solvent, such as chlorine trifluoride–molybdenum hexafluoride, can be so accomplished as to permit the observation of both monomer and complex bands.

P/940. The chemistry of fused salts. Dieter M. Gruen, Robert L. McBeth, Peter Graf and Sherman Fried (U.S.A.).

Fused salts play important roles in many areas of nuclear technology. These include high tem-

perature homogeneous reactors, fuel processing systems, and the production of very pure metals like uranium and thorium. There is little doubt that, in the future, fused salts will find still other applications in the nuclear energy field. A better understanding of the chemistry of fused salt systems is required in order to meet successfully the many challenging problems associated with the practical uses of these materials.

This paper reviews recent work done in the Chemistry Division at Argonne on the chemistry of fused salts, and indicates the directions in which further information is being developed.

1. *Oxidation states*

Oxidation states of many actinide and fission product ions dissolved in fused alkali and alkaline earth nitrates, chlorides and fluorides have been determined for the first time by means of high-temperature spectrophotometry. Information has been obtained concerning relative stabilities of the oxidation states of the same element in different fused salt matrices and of a series of elements in the same matrix.

2. *Co-ordination numbers and complex ion formation.*

Information concerning co-ordination numbers in fused salts has been obtained by comparing absorption spectra of transition metal ions in crystals and in melts. It has been shown that certain molecular groupings (e.g. $CoCl_4^=$ $NiCl_4^=$, $UCl_6^=$, $NpCl_6^=$, $PuCl_6^=$) that are known to exist in crystals are stable also in fused salts even at relatively high temperatures. The spectrophotometric technique has been employed to determine for the first time free energies, heats of formation and entropies of a number of complex ions occurring in fused salts. The implications of these findings to the electrochemical behaviour of melts will be discussed.

3. *Chromatography of fused salts*

An interesting technique for separating metal ions dissolved in fused salts has been developed. Many transition metal ions are adsorbed on γ-Al_2O_3 from nitrate melts. They may be eluted preferentially from the column by adding chloride ion to the melt. The differences in elution rates are due to differences in the stabilities of chloride complexes formed in the melt. Other adsorbing agents and other fused salt systems are under investigation.

4. *Oxidation-reduction reactions*

A number of oxidation-reduction reactions of transition metal ions have been studied primarily in chloride melts. In the uranium chloride–alkali metal chloride system, for example, the thermodynamics of the reactions U (metal) = UCl_3 = UCl_4 = UO_2Cl_2 have been investigated by spectroscopic means. Similar studies on neptunium and plutonium chloride systems are under way. The relation of these studies to electrorefining of metals and fission product separations processes will be discussed.

5. *Acid-base relations*

Fundamental information on acid-base behaviour in fused salts has been obtained spectrophotometrically by means of a colour-indicator method. This information has been used in a study of the thermal decomposition of alkali metal nitrates. The same technique is being employed to investigate neutron damage in molten alkali metal nitrates. The discussion of these reactions will draw attention to the analogous relationship between acid-base and oxidation-reduction reactions in melts.

6. *Chemical reactions in fused salts*

Fused salts present novel media in which to carry out chemical reactions. Among the important reactions to be discussed are (1) the preparation of metals from their salts and (2) the preparation of sulphides and oxides by reaction in and precipitation from fused salts. Other workers both at this and at other laboratories have studied fuel element dissolution and recovery of U from fluoride melts.

P/942. Some recent studies with hexafluorides and halogen fluorides. BERNARD WEINSTOCK (U.S.A.).

NpF_6, the middle member of the actinide triad of hexafluorides, has received relatively little attention in the past and a novel method used for its preparation in gramme quantities will be described. Vapour-pressure measurements with NpF_6 and PuF_6 have yielded the curious result that while NpF_6 is found to be more volatile than UF_6, PuF_6 is found to be less volatile than UF_6. Melting point measurements are found to be more orderly, the value for NpF_6 lying between that for UF_6 and PuF_6. Magnetic susceptibility measurements with NpF_6 show it to exhibit temperature dependent paramagnetism in contrast to both UF_6 and PuF_6 which show only slight second order paramagnetism. The possible relationship between the anomolous vapour-pressure results and the magnetic properties of these compounds will be discussed. The absorption spectrum of NpF_6 vapour and the paramagnetic resonance absorption of solid NpF_6 and dilute solid solutions of NpF_6 in UF_6 have been measured.

OsF_6, the *5d* transition series analogue of PuF_6, has been shown to be identical with the previously reported OsF_6. It appears that an octafluoride has never been prepared. A description of the method of preparation, the proof of composition and some properties of OsF_6 will be given.

The final member of the *5d* transition series of

hexafluorides, PtF_6, has been prepared for the first time, by an unusual technique.

P/1156. Effect of α- and γ-rays on plutonium solutions. M. PAGÈS and M. HAÏSSINSKY (France).

The radiochemical reduction of PuO_2SO_4 has been studied in sulphuric acid solution. On irradiation with ^{60}Co γ-rays, the product first observed is Pu^{IV}. Small amounts of Pu^{III} appear after prolonged irradiation. The yield for reduction to Pu^{IV} in 0·5 N H_2SO_4 solution varies in the usual way with the initial concentration of Pu^{VI}: first increasing with concentration, then becoming independent. The plateau is reached at about $2 \cdot 10^{-2}$ M and the yield is then $G = 1{\cdot}7$.

For an initial concentration of Pu^{VI} equal to $3 \cdot 10^{-3}$ M, $G(Pu^{IV})$ falls from 2 to 1 as the acid concentration increases from 0·1 to 2 N. If the concentration of SO_4^{2-} ions is fixed, however, G moves in the opposite direction, increasing from 0·5 to 1 as (H^+) increases from 0·2 to 0·8 N, then appearing to rise more rapidly for greater acidities. At constant acidity, on the other hand, the yield falls from 2·0 to zero as the SO_4^{2-} concentration is increased from 0·1 to 0·9 M. The effect of SO_4^{2-} is therefore greater than that of H^+ ions.

Self-reduction by plutonium α-rays varies with sulphate and hydrogen-ion concentrations in much the same way as has just been described for ^{60}Co γ-rays with similar G values, in both cases, for the same dissipation of energy. For PuO_2^{2+} concentrations between $5 \cdot 10^{-5}$ and $9 \cdot 10^{-3}$ M, however, the self-reduction yield does not vary with concentration. The reduction in the absence of air and by polonium α-rays is presently being studied.

P/1280. On the separation of Co^{+2} from Co^{+3} ions by the solvent extraction method. S. IONESCU and C. GRIGORESCU-SABĂU (Rumania).

1. A comparative investigation of the extraction of Co^{+2} and Co^{+3} ions in the presence of each other in neutral solution is reported; the *cyclo*hexanol–ether system is of the same separation efficiency as the known systems: amylic alcohol + ether and *iso*amylic alcohol + ether.
2. We propose as a more efficient separation method of these ions, the extraction of Co^{+2} ions as $(Co^{+2}Py_4)(SCN)_2$ with $CHCl_3$. The method can be used also with tracer quantities.
3. The formation of the complex has been investigated by this solvent extraction method varying each of the components in quantity the other being in excess. In this way it was observed that the radiometric titration, with $SCNNH_4$ can be applied successfully to the quantitative determination of Co^{+2}.
4. The equilibrium shift obtained at the titration with pyridine allowed the calculation of the chemical potential for the combination of cobalt with pyridine.

P/1322. Some studies on the tracer chemistry of polonium. KENJIRO KIMURA (Japan).

This report presents some studies in Japan concerning tracer chemistry of polonium.

The polonium compounds with the following reagents were studied: 8-hydroxyquinoline, sodium diethyldithiocarbamate, thenoyltrifluoroacetone, thiourea, sym-diphenylthiourea, thiosemicarbazide, 1-phenylthiosemicarbazide, diphenylcarbazone, diphenylcarbazide, diphenylthiocarbazone and di-β-naphthylthiocarbazone. The results showed that these polonium compounds sublime below 160°C under atmospheric pressure.

The volatility is especially remarkable for the compounds with diphenylcarbazone, diphenylcarbazide and diphenylthiocarbazone.

Above all, the compounds with the first two reagents sublime below 100°C under atmospheric pressure. From the results mentioned above, it follows that the low-temperature sublimation is fairly common to some compounds of polonium.

P/1458. The extraction of actinide elements from wastes. J. S. NAIRN, D. A. COLLINS, H. A. C. MCKAY and A. G. MADDOCK (United Kingdom).

1. As a result of the industrial production of uranium and plutonium, significant quantities of other actinide elements accumulate in wastes, and their recovery has aided investigation of their chemistry. This paper describes methods used to extract gram quantities of ^{230}Th, ^{231}Pa and ^{237}Np from relevant process wastes. The extraction of ^{241}Am from highly irradiated plutonium is also described.

Thorium-230

2. ^{230}Th (alpha half-life 8×10^4 years) exists in secular equilibrium with ^{238}U. A residue, arising during the extraction of uranium from pitchblende and containing 6 p.p.m. ^{230}Th has been processed to yield some tens of grams of ^{230}Th (at an isotopic concentration of 12 per cent with respect to ^{232}Th) by a solvent extraction method involving dibutyl carbitol and tributyl phosphate cycles.

Protactinium-231

3. ^{231}Pa (alpha half-life $\sim 3{\cdot}4 \times 10^4$ years) is a natural decay product of ^{235}U and accumulates in certain residues from plants in which uranium is extracted from ores. Several methods have been successfully used to extract microgram, milligram and gram quantities from a Springfields process residue containing 2–3 p.p.m. ^{231}Pa.

4. Processes are described which involve leaching ^{231}Pa as the stable fluoride complex and its preliminary concentration on a precipitate formed by complexing the fluoride. After treating the precipitate with caustic soda it is dissolved in concentrated HCl and the ^{231}Pa extracted into a solvent such as di-*iso*propylketone. Final purification is achieved by further precipitation and solvent extraction cycles.

5. In a method suitable for small scale work the ^{231}Pa is leached from the residue with concentrated HCl containing some HF and subsequently absorbed as a chloride complex on anion exchange resin after complexing the fluoride. Elution with HCl/HF mixture yields a very pure product.

Neptunium-237

6. ^{237}Np (alpha half-life $2{\cdot}2 \times 10^6$ years) is a by-product of neutron irradiation of uranium. Over 100 g ^{237}Np has been quantitatively recovered from a waste stream containing $<0{\cdot}1$ p.p.m. by a method involving absorption on anion exchange resin. Two anion exchange cycles result in the concentration of ^{237}Np by a factor of 7×10^4. The neptunium is eluted from the resin with dilute nitric acid and further purified from plutonium and uranium by extraction of Np(IV) into TTA/benzene. The final solution of Np(V) nitrate contains about 0·03 per cent ^{239}Pu and less than 0·2 per cent uranium. The overall chemical purity is greater than 99 per cent. Samples of the oxides, the tetrafluorice and the metal have been prepared.

Americium-241

7. ^{241}Am (alpha half-life 470 years) is formed by beta-decay of ^{241}Pu (half-life 13 years) which arises from prolonged neutron irradiation of ^{239}Pu. Pu(IV) is absorbed on anion exchange resin from 8 N HNO_3. ^{241}Am is not retained under these conditions and milligram amounts are periodically "milked" from the column with 8 N HNO_3 as the ^{241}Pu decays. The americium solution is concentrated by evaporation and is purified from uranium by a cycle involving precipitation of americium trifluoride and further separation from uranium using anion exchange techniques in HCl solutions.

P/1471. Tritium production and tritium cycling in a fusion reactor with lithium blanket. ROLF WIDERÖE and KARL O. HINTERMANN (Switzerland).

The reaction $T(d, n)^4He$ has the advantage of a higher reaction cross-section and more energy release compared with the reactions $D(d, p)T$ and $D(d, n)^3He$. Tritium cycle means the use of the neutrons of the (d, n)-reactions in the plasma to produce tritium in a lithium blanket in order to feed again the $T(d, n)^4He$ reaction in the plasma. The efficiency of the blanket is calculated in this paper and the resulting cycle equilibrium rates of the different plasma reactions are computed.

First the slowing down of fast neutrons in lithium is worked out. The result is that the neutrons have a vanishing chance to become thermal, but most of them are involved in a $^6Li(n, \alpha)T$ reaction within a limited energy region. This means a peak in the reaction probability versus energy plot. The energy, where this peak is located, varies with the isotopic ratio of the lithium.

On the other hand the neutrons of each of the two plasma reactions $T(d, n)^4He$ and $D(d, n)^3He$ are monoenergetic apart from Doppler broadening of the plasma temperature and therefore all neutrons involved in the $^6Li(n, \alpha)T$-reaction have similar Fermi ages.

Thus two neutron energy groups are considered namely a fast group and an intermediate group, the latter at the energy where most of the neutrons are absorbed for the reaction with lithium. The spatial flux distribution of the second group within the lithium blanket yields the reaction density distribution.

The efficiency of the process is plotted versus blanket thickness. The relative $T(d, n)^4He$ reaction rate is computed as a function of fuel cycle parameters without addition or withdrawal of tritium to or from the system in steady state conditions. The results for natural lithium and for lithium enriched in the isotope ^6Li are compared.

P/1548. Chemistry and crystallography of uranium oxide systems. HENRY R. HOEKSTRA and STANLEY SIEGEL (U.S.A.).

Uranium oxide systems have been the subject of continued intensive investigation during the past few years. Interest stems, in part, from use of the oxides as high temperature reactor fuels. In addition, many procedures in the preparation and recycling of feed materials for reactors are directly concerned with uranium oxide systems. This paper presents the results of our investigations during the past three years on the uranium-oxygen system, and on several related binary oxide systems. A survey of recent publications by other investigators is included in order to present a complete picture of current work in this field.

Our studies on the structure of U_4O_9 indicate that the oxide may not crystallize in the simple fluorite lattice which has generally been accepted for this compound. The U_3O_8 phase has been shown to have a relatively narrow composition range ($UO_{2\cdot65}$–$UO_{3\cdot667}$) below which it converts to a larger orthorhombic cell whose composition range extends from $UO_{2\cdot56}$ to $UO_{3\cdot03}$. The preparation and some properties of four crystalline modifications of uranium trioxide is described,

as well as methods for interconversion of the structural types. Studies of uranium trioxide hydrates under various conditions of temperature and pressure are included.

Alkali metal uranate systems have been investigated at elevated temperatures and their methods of preparation described. Three compounds have been identified in the sodium oxide–uranium oxide system: $Na_2U_2O_7$, Na_2UO_4 (two crystalline modifications), and Na_4UO_5. Sodium diuranate, previously identified as the monouranate, crystallizes in the orthorhombic system; Na_4UO_5 has a tetragonal structure. No appreciable solid solubility range exists between the phases. The thermal stability increases in the order $Na_4UO_5 < Na_2UO_4 < Na_2U_2O_7$; decomposition seems to occur by volatilization of the alkali metal oxide. Sodium diuranate is stable in aqueous solutions at room temperature, but the other uranates are hydrolysed rapidly. A study of the remaining alkali metal uranate systems indicates that their thermal stability decreases with increasing size of the alkali metal ion. The lithium compound is the only alkali metal monouranate which is stable at 1000°C, and the only monouranate to resist hydrolysis at room temperature.

Other uranate systems which have been investigated to some extent include the zinc and lead compounds. The preparation of zinc and lead uranates and their thermal stability is discussed. Lead uranate is isomorphous with the corresponding barium compound, and can be decomposed to give the binary oxide, $Pb_2U_2O_7$, which appears to crystallize in a fluorite-type structure.

P/1550. Solvent extraction of uranium and other metals by acidic and neutral organophosphorus compounds. C. A. Blake, C. F. Coleman, K. B. Brown and C. F. Baes (U.S.A.).

The properties of a number of new organophosphorus reagents are summarized, and their positions in a new solvent extraction technology are discussed. In contrast to the familiar tributylphosphate (TBP), the applications of which have been limited to highly salted nitrate solutions, several other neutral and acidic organophosphorus compounds have demonstrated the ability to extract uranium from a wide variety of aqueous solutions. Some of these reagents have reached commercial use in recovery of uranium from sulphate and phosphate liquors. More generally, by proper choice of reagent it is now possible to extract uranium from nearly any solution in which it is encountered. In addition, many of these reagents show potentiality for extraction of other metals, including vanadium, thorium, zirconium, hafnium, titanium, molybdenum, rare earths and plutonium, and for separations of closely related elements, including zirconium–hafnium, lanthanides and actinides. Besides process applications, these extractants offer valuable analytical and physicochemical applications, some of which have already been developed.

The reagents described include mono- and di-alkyl esters of *ortho*phosphoric acids, monalkylphosphonic acids, and dialkylphosphinic acids; the neutral esters of these acids; trialkylphosphine oxides; and certain mixtures of the acid with the neutral compounds. Some other related reagents are also noted, including polymerized reagents.

Extractions by the neutral compounds are similar in nature to extractions by TBP. However, complex stabilities increase with replacement of ester by carbon–phosphorus bonds, so that extraction coefficients can be obtained which are up to five orders of magnitude higher than can be achieved with TBP. This greatly increased complex stability suggests use not only in many of the systems where TBP can be used, but also in related systems which are out of the reach of TBP extraction. The phosphine oxides are being increasingly used in analytical applications.

The acid reagents extract metals from acidic solution by exchange of hydrogen ions for the metal ion, and exchange metal ions with neutral and basic solutions. They thus provide a means of applying cation exchange on a liquid–liquid basis, with certain inherent advantages of liquid over solid and of disperse over polymerized extractants. Chemical equilibria in the extractant solutions and in the extraction systems are discussed. Since the acid reagents extract cations rather than neutral or anionic complexes, they are particularly useful for study of aqueous complex formation. A special property of the dialkylphosphoric acids is that their combinations with the neutral organophosphorus reagents show synergistic enhancements of uranium extraction ability, up to 50 times higher than the cumulative abilities of the separate components. Certain of the acid reagents, including synergistic combinations, are currently used in uranium raw materials processing.

In addition to the comparisons of different reagent types, correlations with other properties and the effects of variation of structure within a reagent type are also discussed. These include both general and specific effects on extraction power, selectivity, and physical behaviour, which are of sufficient magnitude to add significantly to the versatility of this wide range of solvent extraction reagents.

P/1605. Anion exchange of metal complexes. The uranyl–phosphate system. Y. Marcus (Israel).

The uranyl (M)–phosphate (A) complex system in acid solution has been studied by an anion exchange method. Batch equilibrations of

Dowex-1 phosphate resin (RA) with phosphoric acid (HA) and tripotassium phosphate–monosodium phosphate (3 : 1) buffer solutions provided data on uranium distribution and phosphate concentration. The activity of phosphate ions in the solution and in the resin was calculated, and "ideal" distribution values, derived from the data, were used by sweeping and "curve fitting" methods for a calculation of the complexity constants by successive approximations. These constants are illustrated by a "predominance area" diagram. The main species found are: MA^+, Ma_2, $M(HA)_2^{++}$, MA_3^-, $M(A, 2HA)^+$ and $M(HA)_2^{++}$ in the solution, and RMA_3 in the resin.

P/1609. The electrodeposition of uranium from monocalcium phosphate solution. E. Foa, Y. Marcus, J. Trocker, I. Alter, J. Lavi, J. Tulipman, Z. Waldman, A. Grunstein and Y. Prulov (Israel).

When phosphate rock is leached by mineral acids under suitable conditions, about 80% of the uranium and 90% of the phosphate of the rock pass into solution, the latter as monocalcium phosphate. Electrolysis of this solution results in the deposition of about 90% of the uranium on the cathode.

The mechanism of this electrodeposition is described, and the various factors which are expected to bear on the efficiency of the process (current density, material and form of the electrodes, etc.), are discussed. The methods for the stripping of the uranium deposits from the cathode are described.

A survey is given of the results achieved with this method on industrial scale.

P/1650. Study of the possibility of preparation of high specific activity ^{60}Co through Szilard–Chalmers reaction. Amar Nath, Jagdish Shankar and S. B. Srivastava (India).

Several chelates of cobalt (III) have been studied. It has been found that great care is necessary in the preparation and purification of the complexes so as to eliminate all traces of cobaltous impurities. The choice of the methods used for the separation of cobalt-60, along with Co(II), has been guided by the ease of manipulation and the necessity to avoid decomposition of the irradiated complex during the process.

The enrichment factor is profoundly influenced by the conditions of neutron irradiation, such as γ-flux and temperature. It also depends on the time which elapses between irradiation and the chemical separation and the temperature at which the sample is stored.

P/1764. Neutron diffraction studies of magnetic structure. J. M. Hastings, N. Elliott, L. M. Corliss and W. C. Hamilton (U.S.A.).

Antiferromagnetism in inorganic compounds is thought to result from exchange interactions between magnetic ions operating through non-magnetic connecting ions. This indirect exchange would be expected to show correlations between magnetic moments of cations bonded to a common anion. More generally, this mechanism should result in a connection between crystal structure and the relative orientation of magnetic dipoles in the antiferromagnetic state. The antiferromagnetic structures of a number of simple and related compounds have been obtained by neutron diffraction in order to test the validity of these ideas and to explore further the dependence of magnetic structure on crystal structure.

Manganous sulphide exists in three polymorphic forms, all of which are antiferromagnetic. The α form is a NaCl arrangement of manganese and sulphur. In the zinc blende and wurtzite forms (β-MnS) each manganese is bonded tetrahedrally through sulphur atoms to its twelve nearest manganese neighbours. The magnetic structures previously observed by us indicate that strong antiferromagnetic correlations exist between second nearest neighbours in α-MnS and between nearest neighbours in the two β forms. Indirect exchange coupling thus appears to involve linear Mn–S–Mn bonds in the first instance and tetrahedral bonds in the second.

Recent neutron diffraction measurements indicate that the mineral chalcopyrite ($CuFeS_2$) is antiferromagnetic at room temperature. Crystallographically the structure is the zinc blende type with an ordered arrangement of cations which places two coppers and two irons in tetrahedral co-ordination about each sulphur. As in the case of the zinc blende form of MnS, the observed magnetic structure results in antiparallel alignment of the two irons tetrahedrally bonded to a common sulphur.

The homologous series of compounds MnS_2, $MnSe_2$, and $MnTe_2$ crystallize with the pyrite structure, which is a NaCl-like arrangement of M and X_2 groups. The orientation of X_2 groups is such as to produce nearly regular tetrahedra with apices occupied by three metal atoms and one member of an X_2 group, and centres occupied by the other member of the X_2 pair. In all cases, nearest neighbour antiferromagnetic correlations are observed, as might be anticipated from the presence of tetrahedral M–X–M linkages. MnS_2 exhibits a magnetic structure identical with that of the zinc blende modification of MnS (ordering of the third kind); $MnTe_2$, a layer structure (ordering of the first kind); and $MnSe_2$, an intermediate structure.

Chromium nitride (CrN), a rock-salt structure, has been found to be antiferromagnetic and to possess the fourth kind of f.c.c. magnetic ordering. As in α-MnS, indirect exchange appears to involve a linear Cr–N–Cr path.

In another application of neutron diffraction, magnetic scattering has made possible the

investigation of the long-standing problem of the nature of the second order phase transition which occurs in magnetite (Fe_3O_4) at 119°K. The great decrease in electrical conductivity which accompanies this transition led Verwey and co-workers to postulate that the transition involves an ordering of ferric and ferrous ions which have a random arrangement above the transition temperature. The problem of verification of this ordering, near impossible by X-ray diffraction, is one which is especially suitable to attack by neutron diffraction methods because of the difference between the magnetic scattering cross-sections of the ferric and ferrous ions. Measurements on synthetic single crystals have unambiguously established the validity of the Verwey ordering scheme.

P/1810. Separation of technetium from rhenium by paper electrophoresis. RODRIGO ALBERTO GUEDES DE CARVALHO (Portugal).

The electrophoretic separation of rhenium from technetium was achieved by reduction of Tc(VII) to Tc(IV) which is cationic or does not migrate, whilst Re(VII) is not affected by the reductant and maintains its anionic character.

Among several reductants studied buffered solutions of hydrazine hydrate and sulphate (pH = 8 to 9), and hydriodic acid permitted very good and rapid separations of the two elements.

P/1832. Ion exchange properties of hydrous oxides. K. A. KRAUS, H. O. PHILLIPS, T. A. CARLSON and J. S. JOHNSON (U.S.A.).

The large class of amorphous insoluble hydrous oxides has interesting ion exchange properties. These materials have high capacities and suitable exchange rates and may therefore be used in packed columns in typical chromatographic (ion exchange) manner.

Hydrous oxides may exhibit either cation exchange or anion exchange properties, or both. The type of adsorption depends on the element on which the oxide is based, on the acidity of the medium and, to some extent, on the ion adsorbed. In general, anion exchange properties become dominant at high acidities, cation exchange properties at lower acidities or in basic solutions, and at some acidities anion exchange and cation exchange capacities may be equal, leading to total salt removal. The most basic oxides may not show significant cation exchange properties, and conversely the very acidic oxides may not show significant anion exchange properties.

Though some of the most acidic oxides are soluble (e.g. P_2O_5) or easily dispersible (e.g. MoO_3, WO_3) their intrinsic cation exchange properties may be utilized by incorporating them in excess into an insoluble matrix, i.e., by preparing certain insoluble acidic salts. This presumably is the basis of the pronounced cation exchange activity of zirconium phosphate, tungstate, molybdate, arsenate, etc.

The selectivities of the hydrous oxides are striking. Some of the materials with cation exchange properties may be used even with extremely small columns for the separation of the alkali metals from each other or of the alkaline earths. The specificity of these compounds for caesium in acidic solutions permits the almost unique isolation of this element from practically all others.

Those oxides with anion exchange properties also have unusual selectivities compared with the organic ion exchangers. They are extremely selective for various polyvalent anions and should find application in the recovery of many metallic anions such as chromate, molybdate, tungstate and arsenate. If the metal on which the oxide is based has unusual complexing properties the resulting solid often reflects these in special selectivities. Thus, oxides based on Bi(III) have high selectivities for the heavier halides and others, such as the oxides of Zr(IV), Nb(V) and Ta(V) for remarkable selectivities for fluorides.

The studies of the hydrous oxides have been concerned so far principally with the characterization of those properties fundamental to their use as ion exchangers or adsorbents. However, these same studies have direct pertinence in other fields, such as corrosion films, catalysis, geochemistry, and general studies of amorphous and micro-crystalline materials.

P/2064. Complex utilization of uranium ores. V. B. SHEVCHENKO, V. A. MIKHAILOV, N. F. KASHCHEEV *et al.* (U.S.S.R.).

The paper describes a method of complex processing of rich uranium ores which provides for the simultaneous extraction of uranium, radium, ionium (thorium-230) and protactinium-231 from the ore. The combination of nitrate leaching operation with uranium extraction by a tributylphosphate solution in an inert diluent is a distinguishing feature of the uranium branch of the process.

P/2099. A contribution to the solution of the structure of U_3O_8. B. CHODURA and J. MALÝ (Czechoslovakia).

The purpose of the paper is to explain the structure of U_3O_8. Three cells alternate in the structure of U_3O_8—one orthorhombic and two monoclinic ones, which are close to being orthorhombic, as was determined by the X-ray method for a rotating monocrystal. This arrangement explains also the superstructure with a threefold parameter $a = 11{\cdot}90$ kX, which was found on all photographs taken around axes *a*, *b* and *c*. A slight double periodicity in the direction of axis

c ($c = 8{\cdot}27$ kX) was observed on the photographs taken around axis c. A probable explanation of the structure is given and the most probable group is derived.

P/2127. Studies in the americium chemistry. G. N. YAKOVLEV and V. N. KOSYAKOV (U.S.S.R.).

During the processing of specially irradiated materials or of waste products after the recovery of nuclear fuels, transplutonium elements are concentrated together with the rare-earth fraction of the fission products. Further separation encounters considerable systematic and technological difficulties due to the great specific activity of the products being processed. At the present time much attention is given to the development and choice of technological and analytic techniques for the most simple and economic chemical separation of these elements.

A number of methods are known for the separation of americium and curium, including precipitation reactions and extraction and chromatographic methods. New data obtained during the study of some of these processes are presented and discussed.

P/2216. Separation of uranium and plutonium from fission products by a mixture of dibutyl ether and carbon tetrachloride. V. M. VDOVENKO *et al.* (U.S.S.R.).

A description is given of an extraction technique for processing irradiated uranium. The solvent is an explosion-proof mixture of dibutyl ether and carbon tetrachloride. After co-extraction of hexavalent uranium and plutonium nitrates so that the bulk of fission elements remains in the aqueous waste solution, plutonium is separated from uranium by reductive re-extraction. Further purification of plutonium is carried out in a 2-cycle extraction-re-extraction process. The separation of uranium from fission products is carried out in a 1-cycle operation.

Summary purification from fission product gamma-activity

$$U: 1{\cdot}2 \cdot 10^6,$$
$$Pu: 8 \cdot 10^4$$

Uranium recovery yield is 99·9%; plutonium yield is 98%.

P/2247. Basic applications of chemistry in atomic energy—Recent advances in the basic chemistry of plutonium, americium and curium. L. B. ASPREY, T. K. KEENAN, T. W. NEWTON and S. W. RABIDEAU (U.S.A.).

The major advances in fundamental plutonium chemistry have arisen from investigations of the kinetic and the equilibrium aspects of aqueous oxidation-reduction reactions. The oxidation-reduction potentials of plutonium ions in acid solutions have been determined precisely, enabling the accurate estimation of many equilibria to be made. The principal advances in the chemistry of americium and curium have been the discovery and the isolation of new valence states and the characterization of metals and compounds. Some new purification procedures have been developed.

Equilibrium studies. Equilibrium relationships among the aqueous plutonium species were obtained from electromotive force, spectrophotometric and kinetic data.

Thermodynamic quantities for the Pu(III)–Pu(IV) and the Pu(V)–Pu(VI) couples were obtained as a function of temperature. The formal potentials of the Pu(III)–Pu(VI) couples were obtained as a function of temperature by a combination of the Pu(III)–Pu(IV) potentials with the Pu(IV) disproportionation equilibrium quotient, $Pu(VI)\ Pu(III)^2\ (H^+)^4/Pu(IV)^3$. The temperature coefficient of this equilibrium quotient was obtained from the rate of disproportionation of Pu(IV). The hydrolysis quotient of Pu(IV) and its temperature coefficient were obtained from the Pu(III)–Pu(IV) couple at varied acidities.

Equilibrium quotients for the rapid reversible reaction, $Pu(IV) + Pu(V) = Pu(III) + Pu(VI)$, were obtained kinetically as a function of temperature from $-d(Pu(VI))/d^n$ data in perchloric and in deutero perchloric acid solutions. The values of the equilibrium quotient derived kinetically agree with those obtained from the Pu(III–)Pu(IV) and the Pu(V)–Pu(VI) potentials.

Formation equilibrium quotients have been determined for the chloro complexes of Pu(III), Am(III) and Cm(III), for the hydroxy, nitrate and sulphate complexes of Pu(IV) and for the chloro complexes of Pu(VI).

Kinetic studies. Studies were made involving reactions between plutonium species with each other, with oxygen, V(III) and U(IV). Rate laws including hydrogen ion concentration dependences and temperature coefficients were determined.

Reduction of Pu(VI) to give Pu(V) was studied with: (1) Pu(III); (2) V(III); and (3) U(IV). These reactions are fast and first order in both reactants. The hydrogen ion concentration dependence for (1) is zero and is predominantly inverse first for (2) and (3). Reaction (3) shows evidence for a metastable intermediate.

The Pu(III)–Pu(IV) exchange reaction is very fast, first order in each reactant and predominantly inverse first in hydrogen ion concentration.

The disproportionation reactions of pentavalent plutonium and americium have been investigated. In both cases initial steps have been found to be $2M(V) = M(IV) + M(VI)$; however, the hydrogen ion concentration dependences are different. The initial step for Pu(IV) disproportionation is $2Pu(IV) = Pu(III) - Pu(V)$.

The reaction between Pu(III) and O_2 is fast, second order in Pu(III), first order in oxygen, and essentially zero power in hydrogen ion concentration. The rate is strongly dependent upon the sulphate ion concentration and indicates two parallel paths involving two and three sulphates.

The effects of alpha self-irradiation of aqueous plutonium and americium solutions include reduction of oxidation state, inhibition of reduction by chloride ion and formation of hydrogen peroxide.

Solid phase studies. The existence of two forms of americium metal has been established. A double hexagonal close-packed phase, stable at lower temperatures, has been determined by X-ray studies. Evidence for existence of a higher temperature face-centered cubic structure has also been obtained. Attempts to elucidate the structure of curium metal even when using the longer lived curium-244 have thus far not met with success.

An investigation of the stability of divalent americium and curium as chlorides has been made. The preparation of curium tetrafluoride and determination of its structure have unequivocally demonstrated the existence of tetravalent curium. Intensive efforts to produce an oxidation state of curium higher than three in either alkaline or acidic aqueous media gave no evidence of oxidation when using curium-244.

The absorption spectra of solid tetrafluorides of americium and curium have also been measured. Examination of the spectrum of aqueous trivalent curium and the solid trifluoride has revealed the presence of prominent characteristic absorption peaks previously unreported. Studies of the fluorescence spectrum of curium trifluoride in a lanthanum trichloride matrix have confirmed the existence and position of these peaks.

New measurements of the magnetic susceptibilities of plutonium, americium and curium compounds have been reported.

P/6. Fission processes in the proton bombardment of ^{232}Th ^{238}U and ^{239}Pu. J. P. BUTLER, B. J. BOWLES and F. BROWN (United Kingdom).

P/31. The significance of certain complexes of ruthenium, niobium, zirconium and uranium in plant processes. P. G. M. BROWN, J. M. FLETCHER, C. J. HARDY, J. KENNEDY, D. SCARGILL and A. G. WAIN (United Kingdom).

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PUBLISHERS' NOTICE

Mr. H. A. C. McKay will be taking up an appointment abroad, and in consequence has had to relinquish his editorship of the Journal.

Upon the advice and suggestions of the Honorary Editorial Advisory Board and the Board of Editors of the Journal, the following appointments have been made:

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The Publishers would like to express their warmfelt gratitude and appreciation for the many years' service that Mr. McKay has rendered to the Journal.

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BRANCHING IN THE DECAY OF ^{97}Ru TO ^{97m}Tc AND ^{97}Tc

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(*Received* 4 *February* 1958)

Abstract—By comparing the *K* X-ray intensity of 90 day ^{97m}Tc with the *K* X-ray intensity of the 2·88 day ^{97}Ru parent from which it grew, we found that ^{97}Ru branches 0·041 ± 0·005 per cent to ^{97m}Tc and 99·96 per cent to ^{97}Tc. Based on this measurement and data in the literature, a revised decay scheme is proposed for ^{97}Ru. Analysis of fourteen decay curves showed a half-life of 2·88 ± 0·04 days for ^{97}Ru.

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FOR a determination[1] of the half-life of the ^{97}Tc ground state it became necessary to measure the branching ratio of ^{97}Ru to form the two ^{97}Tc isomers. It had been generally assumed[2] that ^{97}Ru decays mostly to the 90 day metastable state, ^{97m}Tc. Based on this supposition, spin and parity assignments were made[2] to the ground state of ^{97}Ru and to excited states of ^{97}Tc. The present investigation shows that only 0·041 per cent of ^{97}Ru disintegrations are to 90 day ^{97m}Tc. This result was obtained by comparing the *K* X-ray intensities of ^{97}Ru samples with the corresponding X-rays from internal conversion in the ^{97m}Tc which grew from these Ru samples.

EXPERIMENTAL PROCEDURE AND RESULTS

Two irradiations of Ru metal powder were performed with 11 MeV deuterons in order to prepare 32 min ^{97}Rh from which pure 2·88 day ^{97}Ru could be "milked". For the most intense irradiation 150 mg of Ru was bombarded with a 40 μA beam of deuterons for 30 min. The Ru target was dissolved in 5% NaOCl solution, $NaBiO_3$ was added, and the RuO_4 distilled with $HClO_4$. The 32 min ^{97}Rh remained behind in the distilling flask. Then more Ru carrier, $NaBiO_3$, and $HClO_4$ were added to the flask, and the RuO_4 was distilled over. This operation was completed 60 min after end of the irradiation. Both of these RuO_4 distillates were discarded. After allowing about 1·5 hr for 2·88 day ^{97}Ru to grow in from its 32 min Rh parent, Ru carrier, $HClO_4$, and $NaBiO_3$ were again added to the flask, and a third distillation was carried out. This distillate was retained and the Ru therein was purified by another distillation, two precipitations from basic solution after reduction with ethanol, and finally precipitation as the metal from HCl solution by reduction with Mg.

The Tc *K* X-ray intensity from orbital electron capture in the ^{97}Ru samples was followed with a 4-in. diameter, 2 atm, argon filled proportional counter connected to a single channel analyser. The most intense sample decayed from 28,000 counts/min in the *K* X-ray peak to nearly background with a half-life of 2·9 days. If the ^{97}Ru had all decayed to the 90 day ^{97m}Tc isomer one would expect to find 600 counts/min of Tc *K* X-rays resulting from nearly 100 per cent internal conversion[3] of a 96·5 keV

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[1] S. KATCOFF, *Phys. Rev.* In press. The ground state half-life is (2·6 ± 0·4) × 10^6 years.
[2] J. M. CORK, M. K. BRICE, L. C. SCHMID and R. G. HELMER, *Phys. Rev.* **100**, 188 (1955).
[3] G. E. BOYD, *Phys. Rev.* **95**, 113 (1954).

isomeric transition between ^{97m}Tc and ^{97}Tc. Actually, only an upper limit of 5 counts/min was observed; this established an upper limit of 0·8 per cent for the branching of ^{97}Ru to ^{97m}Tc.

In three subsequent experiments 100 mg samples of Ru were irradiated in the Brookhaven pile for times between 0·6 and 1·9 days at a neutron flux of about 3×10^{12} per cm^2 sec. In these cases 2·88 day ^{97}Ru was produced by (n,γ) on ^{96}Ru. However, 40 day ^{103}Ru was also produced in considerable yield from ^{102}Ru. The ^{103}Ru decays to 57 min ^{103m}Rh which emits some Rh K X-rays (20·2 keV) that are not sufficiently resolved from Tc K X-rays (18·4 keV). In practice, it was found that the 2·88 day ^{97}Ru K X-ray intensity could be determined by analysis of the decay curve. However, in order to measure the intensity of the K X-rays from 90 day ^{97m}Tc it was necessary to separate the Tc chemically from an aliquot of the Ru following decay of 2·88 day ^{97}Ru.

After initial solution of an irradiated Ru sample, a small aliquot was purified by the method outlined above. The remainder of the Ru was allowed to stand about a week for additional ^{97m}Tc to grow in. Then some 6·0 hr ^{99m}Tc tracer activity* was added so that the chemical yield of the ^{97m}Tc could be determined following its separation and purification from the Ru. This procedure included two successive distillations of Tc_2O_7 with concentrated H_2SO_4, one $Ru_2O_3 + RuO_2$ scavenging precipitation, two $Fe(OH)_3$ scavenging precipitations, elution of $(TcO_4)^-$ from a Dowex-1 anion exchange column† with 0·2 N $HClO_4$, and co-precipitation of Tc_2S_7 with about 2 mg of CuS.

All of the Tc samples showed an initial decay with a half-life of 4·2 days characteristic of ^{96}Tc. This must have been formed from ^{96}Ru by (n,p) reaction. After decay of this component the small amount of residual activity was presumably from 90 day ^{97m}Tc. Only in the last of these three runs was there sufficient activity ($\sim$17 counts/min) to identify the ^{97m}Tc by its half-life. The experimental value was 86 ± 9 days. It is possible that part of the observed activity was from 60 day ^{95m}Tc. Therefore the branching ratios derived from this set of runs may be somewhat high, but an upper limit of 0·05 per cent is established. Table 1 summarizes the data. Calculation of the activity expected of 90 day ^{97m}Tc if all of the ^{97}Ru decayed to it was by means of the following equation:

$$A_2 = A_1^0\left[\frac{\lambda_2}{\lambda_2 - \lambda_1}\, e^{-\lambda_1 t} + \frac{\lambda_1}{\lambda_1 - \lambda_2}\,\frac{(1 - e^{-\lambda_2 \tau})}{(1 - e^{-\lambda_1 \tau})}\, e^{-\lambda_2 t}\right]$$

where A_2 is the activity of ^{97m}Tc after an irradiation time τ followed by a time t during which the ^{97m}Tc grows from its ^{97}Ru parent; A_1^0 is the activity of ^{97}Ru at the end of the irradiation; λ_1 and λ_2 are the disintegration constants of ^{97}Ru and ^{97m}Tc, respectively. No corrections were necessary for counter efficiency or for K fluorescence yield because both ^{97}Ru and the ^{97m}Tc isomeric transition give rise to Tc K X-rays. It was assumed that internal conversion in the decay of ^{97}Ru to states other than ^{97m}Tc was small and contributed little to the K X-ray intensity.

A final pair of experiments was performed which eliminated any uncertainty due

* This was prepared by "milking" from 66 hr ^{99}Mo which had been prepared by neutron activation in the pile. The characteristic 140 keV γ-ray of ^{99m}Tc was used to follow the progress of the Tc during the purification.

† The first of these three experiments did not include the anion exchange step.

to 60 day ^{95m}Tc and which gave considerably more 90 day ^{97m}Tc activity. In each of these runs the entire amount of Ru was purified three days after the irradiation. Two aliquots were then removed: one for ^{97}Ru measurements and one for growth of 90 day ^{97m}Tc daughter activity. The latter aliquot was further purified from technetium by adding H_2SO_4 and distilling out any Tc_2O_7. Then, after allowing 7 days for 90 day ^{97m}Tc to grow in from its 2·88 day ^{97}Ru parent, more H_2SO_4 was added and the Tc_2O_7 was distilled. Purification of Tc was completed by means of a redistillation with H_2SO_4, scavenging precipitations with $Fe(OH)_3$, anion exchange separation,

TABLE 1.—DATA FOR ^{97}Ru BRANCHING RATIO; THREE PRELIMINARY EXPERIMENTS

Run	3	4	5
Observed ^{97}Ru *K* X-rays corr. to end of bombardment (counts/min)	76,000	78,000	124,000
Geometry correction	17·6	17·6	17·6
Self absorption correction	1·06	1·02	1·07
Aliquot factor	3·25	24·3	7·48
Correction for *L*-capture[4]	1·107	1·107	1·107
Corrected ^{97}Ru activity at end of bombardment, A_1^0	$5{\cdot}1 \times 10^6$	$3{\cdot}77 \times 10^7$	$1{\cdot}93 \times 10^7$
Expected ^{97m}Tc after time $(\tau + t)$ for 100% branch, A_2	$1{\cdot}42 \times 10^5$	$1{\cdot}22 \times 10^6$	$6{\cdot}0 \times 10^5$
Irradiation time, τ (days)	0·605	1·94	1·27
Growth time, t (days)	7·5	6·75	8·3
Observed ^{97m}Tc *K* X-rays at t (counts/min)	7	4	24
Chemical yield of ^{97m}Tc (%)	17·6	1·3	11·2
Correction for *L*-conversion in ^{97m}Tc[3,5]	1·61	1·61	1·61
Corrected ^{97m}Tc at t (counts/min)	64	500	340
Branching ratio	$4{\cdot}5 \times 10^{-4}$	$4{\cdot}1 \times 10^{-4}$	$5{\cdot}7 \times 10^{-4}$

and co-precipitations with CuS. Chemical yields were measured with the aid of 6·0 hr ^{99m}Tc tracer. After decay of the 6·0 hr period, the Tc samples from both runs decayed with a half-life of 91 ± 3 days and the X-rays were shown to be characteristic of Tc by means of critical absorbers.

The data and results are given in Table 2. The average value of the branching ratio, $(4{\cdot}1 \pm 0{\cdot}5) \times 10^{-4}$, is in good agreement with the results of the three preliminary runs (Table 1). The calculation of the 90 day ^{97m}Tc activity to be expected for 100 per cent branching to it was calculated from the following:

$$A_2 = A_1^0 \frac{\lambda_2}{\lambda_2 - \lambda_1} (e^{-\lambda_1 t} - e^{-\lambda_2 t})$$

where A_2 is the activity of ^{97m}Tc grown from an initial activity A_1^0 of ^{97}Ru in time t; λ_1 and λ_2 are the decay constants of ^{97}Ru and ^{97m}Tc, respectively. The corrections that were applied are similar to those described above.

The decay of all the Ru samples was followed by means of the X-ray proportional counter spectrometer, a scintillation counter, and an end-window proportional

[4] M. E. ROSE and J. L. JACKSON, *Phys. Rev.* **76**, 1540 (1949).

TABLE 2.—DATA FOR ^{97}Ru BRANCHING RATIO; TWO FINAL EXPERIMENTS

Run	6	7	Run	6	7
Initial observed ^{97}Ru K X-rays (counts/min)	13,800	30,700	Time of growth, t (days)	6·75	7·65
Geometry correction	17·6	1·00	Observed ^{97m}Tc K X-rays at t (counts/min)	88	95·5
Aliquot factor	90·0	1200	Chemical yield of ^{97m}Tc (%)	66·4	31·6
Correction for L-capture[4]	1·107	1·107	Correction for L-conversion in ^{97m}Tc[3,5]	1·61	1·61
Corrected initial ^{97}Ru activity, A_1^0 (counts/min)	$2{\cdot}42 \times 10^7$	$4{\cdot}08 \times 10^7$	Corrected ^{97m}Tc activity at t (counts/min)	213	486
Expected ^{97m}Tc at time t for 100% branch, A_2 (counts/min)	$5{\cdot}98 \times 10^5$	$10{\cdot}5 \times 10^5$	Branching ratio	$3{\cdot}6 \times 10^{-4}$	$4{\cdot}6 \times 10^{-4}$
			Average branching	$(4{\cdot}1 \pm 0{\cdot}5) \times 10^{-4}$	

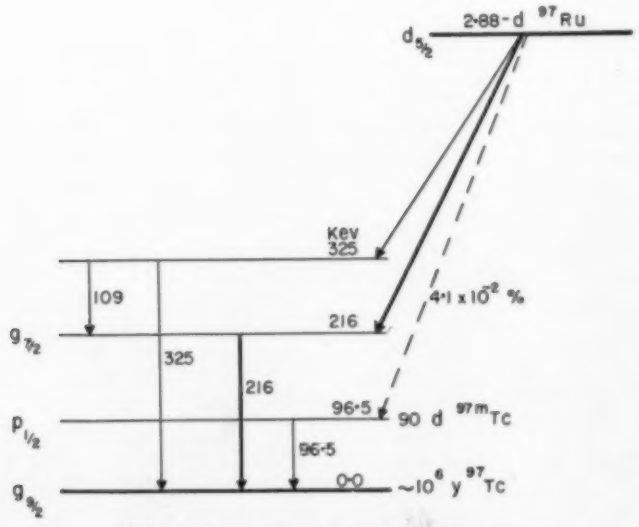

FIG. 1.—Decay scheme proposed for ^{97}Ru. The half-life of ^{97}Tc is $2{\cdot}6 \times 10^6$ years

counter. A weighted average based on the analysis of fourteen decay curves yielded a value of 2·88 ± 0·04 days for the half-life of ^{97}Ru. The samples obtained by "milking" from the 32 min ^{97}Rh were the best and could be followed for about ten half-lives.

DISCUSSION

In view of the very low branching ratio to the 90 day ^{97m}Tc isomeric state which was found in these experiments it is now necessary to revise the nuclear level scheme proposed by CORK *et al.*[2] The 216 keV and 325 keV γ-ray transitions must be to the $g_{9/2}$ ground state of ^{97}Tc rather than to the $p_{1/2}$ 90 day isomeric level (Fig. 1). Direct K capture transition of ^{97}Ru to the ^{97}Tc ground state is shown to be small by the observation that the X-ray intensity was about equal to the γ-ray intensity. Thus a choice can be made between two possible shell model assignments, $d_{5/2}$ and $g_{7/2}$, for the ^{97}Ru ground state: the $g_{7/2}$ assignment must be ruled out because it would require an intense transition to the $g_{9/2}$ ground state of ^{97}Tc; a $d_{5/2}$ assignment to ^{97}Ru appears to be correct. The 90 day isomeric state is probably populated by a 0·041 per cent branch directly from the ^{97}Ru rather than through an intermediate excited level of ^{97}Tc. This conclusion is based on consideration of the probable (ft) value, the measured partial disintegration constant, and the approximate energy of the transition. Fig. 1 shows only one transition (96·5 keV) in the decay of 90 day ^{97m}Tc rather than the three of CORK *et al.*[2] because the two extra lines were not confirmed by other workers.[3,5–7] The very weak 570 keV γ-ray has been omitted from the figure because its location in the level scheme is uncertain.

Acknowledgement—This research was carried out under the auspices of the U.S. Atomic Energy Commission.

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NEUTRON ACTIVATION CROSS-SECTIONS OF ^{96}Ru AND ^{102}Ru

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Abstract—Measurements of the activities of 2·88 day ^{97}Ru and 39·7 day ^{103}Ru from (n,γ) reactions on natural Ru showed that the thermal neutron activation cross-sections of ^{96}Ru and ^{102}Ru are 0·210 and 1·50 barns, respectively. The intensities of 2·70 day ^{198}Au in gold monitors were used as standards. That ^{196}Ru has at least one large resonance in the epithermal region is indicated by cadmium difference measurements. Duplicate runs were reproducible to about 3 per cent but the absolute accuracy is estimated as ±15 per cent.

IN recent compilations[1] the thermal neutron activation cross-section of ^{96}Ru is given as 0·01 barn for the formation of ^{97}Ru. This value was derived from an earlier compilation of WAY and HAINES[2] where reference is made to the work of BOYD and MOTTA.[3] However, these authors reported[3] a ^{96}Ru cross-section of 0·001 barn for production of 90 day ^{97m}Tc, a daughter product of 2·88 day ^{97}Ru. The latter has recently been shown[4] to decay primarily (99·96 per cent) to the ground state of ^{97}Tc. Therefore a new determination of the thermal neutron cross-section of ^{96}Ru was made by measurements of the amount of 2·88 day ^{97}Ru formed from natural Ru. The samples used in this investigations were also used to determine the cross-section of ^{102}Ru from the amount of 39·7 day ^{103}Ru present after decay of the ^{97}Ru.

EXPERIMENTAL PROCEDURE

The irradiations of ruthenium in the Brookhaven reactor were the same as those described previously.[4] Small gold monitors, 5·25 μg, were irradiated simultaneously in the same neutron flux. The Ru was purified and the *K*-rays were measured with an argon-filled proportional counter.[4] Small aliquots, $4{\cdot}20 \times 10^{-3}$ μg, of the gold were measured in a 4π counter and decay of the samples was followed. The data are summarized in Table 1. Correction for the activity produced by epithermal and fast neutrons was made by means of irradiations with cadmium-covered samples of Ru and Au placed in equivalent positions in the pile.

The ^{103}Ru disintegration rates were determined from the observed intensities of Rh *K* X-rays which arise mainly from the 57 min ^{103m}Rh in equilibrium with the 39·7 day ^{103}Ru. DE RAAD *et al.*[7] have measured the ratio of intensities of these Rh *K* X-rays

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[1] D. J. HUGHES and J. A. HARVEY, *Neutron Cross Sections, Brookhaven National Laboratory Report* BNL-325, (1955); General Electric Co. *Chart of the Nuclides* (April 1956).
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TABLE 1.—DATA FOR CALCULATING CROSS-SECTIONS OF ^{96}Ru AND ^{102}Ru

	Run		
	4	5	6
Irradiation time	1·94 days	1·27 days	3·33 days
^{197}Au atoms in aliquot, N_1	$1·28 \times 10^{12}$	$1·28 \times 10^{12}$	$1·28 \times 10^{12}$
Observed ^{198}Au activity in 4π counter 5·6 days after end of bombardment*	27,000 c/min†	13,700 c/min	37,000 c/min
Saturation activity of ^{198}Au	$2·85 \times 10^5$ d/min‡	$2·04 \times 10^5$ d/min	$2·66 \times 10^5$ d/min
^{96}Ru atoms in sample	$0·982 \times 10^{18}$	$3·16 \times 10^{18}$	$0·283 \times 10^{18}$
Observed ^{97}Ru K X-rays 5·6 days after end of bombardment	20,000 c/min	31,000 c/min	7730 c/min
Thermal activation/total activ., ^{97}Ru	0·404	0·404	0·404
Corr. for L-capture, ^{97}Ru	1·107[5]	1·107[5]	1·107[5]
K fluorescence yield, ^{97}Ru	0·78[6]	0·78[6]	0·78[6]
Fraction of K X-rays absorbed in counter gas, ^{97}Ru	0·300	0·300	0·300
Solid angle	0·00874	0·00874	0·00874
Self absorption correction	1·02	1·07	1·00
Corrected ^{97}Ru activity	$4·47 \times 10^6$ d/min	$7·28 \times 10^6$ d/min	$1·69 \times 10^6$ d/min
^{102}Ru atoms in sample	$5·54 \times 10^{16}$	$17·83 \times 10^{16}$	$1·60 \times 10^{16}$
Observed Rh K X-rays 40 days after end of bombardment	5310 c/min	8580 c/min	2660 c/min
Thermal activation/total activ., ^{103}Ru	0·86	0·86	0·86
Rh K X-rays per ^{103}Ru disintegration	0·076	0·076	0·076
Fraction of Rh K X-rays absorbed in counter gas	0·240	0·240	0·240
Saturation activity of ^{103}Ru	$1·76 \times 10^9$ d/min	$4·52 \times 10^9$ d/min	$0·508 \times 10^9$ d/min

* For each run the ^{198}Au formed by epithermal neutrons was measured and subtracted from the total. Thermal activation/total activation = 0·58.

† Counts per minute.

‡ Disintegrations per minute.

to the 498 keV γ-ray (the major γ-ray in the decay of ^{103}Ru). By using a value of 90 per cent for the abundance[7,8] of this γ-ray, one finds that DE RAAD's measurement gives a value of 0·082 Rh K X-rays per ^{103}Ru disintegration. This number was checked in the present investigation by comparing the intensities of the 498 keV γ-rays from two ^{103}Ru sources with the intensity of the 511 keV annihilation radiation from a ^{22}Na source. Photopeak intensities in a 3 in. × 3 in. NaI crystal were measured with a scintillation spectrometer. The ^{22}Na was calibrated absolutely by means of

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[7] B. DE RAAD, W. C. MIDDELKOOP, B. VAN NOOYEN and P. M. ENDT, *Physica* **20**, 1278 (1954).
[8] B. SARAF, *Phys. Rev.* **97**, 715 (1955).

β–γ coincidence counting. The two samples gave values of 0·077 and 0·074, respectively, for the K X-rays per ^{103}Ru disintegration, about 8 per cent lower than the value reported by DE RAAD *et al.*[7] The average, 0·076, was used for calculating the ^{102}Ru cross-section.

RESULTS AND DISCUSSION

The results of the cross-section measurements are given in Table 2. The estimated absolute accuracy is $\pm$15 per cent. It is seen that the ^{96}Ru thermal neutron absorption cross-section, 0·210 barn, is much larger than thought previously.[1–3] This is due

TABLE 2.—THERMAL NEUTRON ACTIVATION CROSS-SECTIONS IN BARNS

Run	4	5	6	Average
$\sigma(^{96}\text{Ru})$, thermal	0·213	0·213	0·205	0·210
$\sigma(^{102}\text{Ru})$, thermal	1·41	1·57	1·52	1·50

mainly to the low branching ratio,[4] $4{\cdot}1 \times 10^{-4}$, to form 90 day ^{97m}Tc. The effective thermal neutron activation cross-section for the formation of ^{97m}Tc is $0{\cdot}21 \times 4{\cdot}1 \times 10^{-4} = 8{\cdot}6 \times 10^{-5}$ barn.

Cadmium difference measurements showed that ^{96}Ru must have at least one strong resonance in the epithermal region because the cadmium cover reduced the ^{97}Ru activity by only 40 per cent while the ^{103}Ru activity was reduced by 86 per cent. Even with gold, which has a strong resonance at 5 eV, the cadmium cover reduced the activation by 58 per cent. Thus it is very likely that one or more of the four resonances (at 9·8, 15·2, 24·1, and 40·9 eV) observed in natural ruthenium by slow neutron velocity spectrometer studies[9] are due to ^{96}Ru.

The cross-section found for ^{102}Ru, $1{\cdot}50 \pm 0{\cdot}22$ barns, is in fair agreement with the old value in the literature[1,10] of $1{\cdot}2 \pm 0{\cdot}3$ barns.

Acknowledgement—This research was carried out under the auspices of the U.S. Atomic Energy Commission.

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ELECTRON CAPTURE HALF-LIFE OF ^{243}Cm

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Abstract—A sample containing ^{243}Cm was milked for Am after a known growth period. From the relative activity intensities and mass ratios in the curium sample and the amount of ^{243}Am which grew in, a value of $1{\cdot}0 \pm 0{\cdot}1 \times 10^4$ years was calculated for the electron capture half-life of ^{243}Cm.

CALCULATIONS of closed decay-energy cycles[1] predict equal masses for ^{243}Am and ^{243}Cm, leaving unresolved the direction of β-decay emission between these neighbouring isobars. A previous attempt to milk ^{243}Am from a sample of ^{243}Cm produced negative results and a lower limit of 50,000 years was set for the electron-capture half-life of

TABLE 1

Isotope	Relative activity	Relative weights
^{242}Cm	1·00	—
^{243}Cm	3·01	2·43
^{244}Cm	1·95	1·00

^{243}Cm.[2] However, that experiment was performed in the presence of relatively large amounts of ^{241}Am and with cruder chemical separation techniques than are presently available. For the present investigation, a sample of curium was used that had been prepared by successive neutron capture in ^{241}Am using the NRX reactor. The curium was purified initially in March 1951, and this plus later purifications ensured complete removal of all americium isotopes from the curium.

Following a growth period of almost 10 months after the last purification, the curium was milked for ^{243}Am. Isotopically pure ^{241}Am was added as a chemical-yield tracer prior to the separations. Three successive elutions from Dowex-50 cation resin using ammonium α-hydroxy*iso*butyrate as eluant[3] were necessary for removal of all the parent curium. The americium fraction was then electroplated by a previously described method[4] to obtain a thin sample for pulse-height analysis. The ratio of ^{243}Am to ^{241}Am was determined in a 50-channel differential pulse-height analyser and the total amount of ^{243}Am calculated from the initial amount of ^{241}Am activity added.

Table 1 gives the relative activity intensities of the curium isotopes obtained from

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an α-particle spectrograph[5] and the relative weights obtained from a mass spectrometer.[6]

These data can be used with the best value for the half-life of ^{244}Cm (18·4 ± 0·5 years)[7] to obtain an α-half-life for ^{243}Cm of 29·0 ± 0·8 years.

In a similar manner the electron-capture half-life of ^{243}Cm can be calculated from the expression

$$t_{1/2_{63}} = 0{\cdot}693\Delta t \frac{N_{63}}{N_{53}},$$

where Δt represents the time of ^{243}Am growth (0·821 years), 63 refers to ^{243}Cm and 53 refers to ^{243}Am. N_{63} was obtained by use of the 29·0-year value given above and N_{53} by use of a value of 7951 ± 48 years[8] for the ^{243}Am half-life. From $2{\cdot}2 \times 10^7$ dis/min of ^{243}Cm, 4·10 dis/min of ^{243}Am was milked. The half-life calculated for electron capture in ^{243}Cm was $1{\cdot}0 \pm 0{\cdot}1 \times 10^4$ years. The errors reported are based upon the estimated half-life errors in ^{244}Cm and ^{243}Am and the errors in counting and assaying.

Acknowledgement—This work was performed under the auspices of the United States Atomic Energy Commission.

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THE SPECIFIC ACTIVITIES AND HALF LIVES OF AMERICIUM-241 AND AMERICIUM-243*

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(*Received* 27 *January* 1958)

Abstract—The specific activities of one sample of ^{241}Am metal and two samples of ^{243}Am metal have been measured. Half-lives of 457·7 ± 1·8 years and 7951 ± 48 years, respectively, have been obtained.

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ALL the values of the half-life of americium-243 published heretofore have been based on determining, by means of an α-ray spectrograph or α-pulse analyser, the relative numbers of ^{241}Am and ^{243}Am alpha particles originating from a sample of americium in which the mass ratio of the two isotopes is known. The determinations have yielded two nonconcordant values for the half-life: 7600 years[1,2] and 8600 years.[2,3] The smallest estimated uncertainty in these determinations is ±370 years, or about 5 per cent. A determination of the half-life by a specific-activity measurement should reduce the estimated error and thus lead to a more reliable value of the half-life. As a result of the americium crystal structure work done in this laboratory[4] we had available one piece of metallic americium-241 and two pieces of metallic americium-243 suitable for a specific-activity determination for each isotope.

An attempt was made to determine the specific-activities of ^{241}Am and ^{243}Am using the compound AmF_3. However, it was found that the extremely erratic results always gave a shorter half-life. This could arise from the formation of AmOF during the drying of the trifluoride; indeed, subsequent work has indicated that americium trifluoride prepared under similar conditions to those used for the specific-activity determinations does incorporate a variable amount of water in the AmF_3, and this could result in hydrolysis during drying. This fact and the difficulty of obtaining consistent impurity corrections have rendered the fluoride data so unreliable that they are not included here.

The specific-activity of ^{243}Am was measured by weighing and dissolving ^{243}Am metal. A check on the technique was made, using ^{241}Am metal. The metals were prepared by reduction of AmF_3 with barium in a tantalum crucible system heated in high vacuum.[4] All of each sample of metal was dissolved, so that no spectrographic analysis on the actual metal used was possible. However, spectrographic analysis on metal similarly produced from the same starting materials showed 0·1 to 0·2 per cent metallic impurities. An impurity content in the metals of 0·15 per cent was

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assumed in calculating all the results. Mass-spectrographic analysis indicated $<0{\cdot}015$ per cent ^{243}Am in the americium-241 and 0·03 per cent ^{241}Am in the americium-243. The metals were scraped free of slag resulting from the reduction and weighed in quartz cones on a quartz fibre torsion microbalance calibrated to $\pm 0{\cdot}1$ per cent. The weighed piece of metal was placed in a weighed 5 ml volumetric flask, dissolved by addition of acid, and diluted to a suitable volume by adding a solution of 6M H_2SO_4 –2M HNO_3. This solution was chosen because there was no detectable change in weight of an aliquot over the length of time necessary to weigh the aliquot. These

TABLE 1

Sample	Specific-activity (alpha disintegration/min/μg)	Half-life (years)
^{241}Am	$(7{\cdot}194 \pm 0{\cdot}029) \times 10^6$	$457{\cdot}7 \pm 1{\cdot}8$
^{243}Am (1st sample)	$4{\cdot}113 \times 10^5$	7939
^{243}Am (2nd sample)	$4{\cdot}100 \times 10^5$	7964
^{243}Am average	$(4{\cdot}107 \pm 0{\cdot}025) \times 10^5$	7951 ± 48

gravimetric aliquots of the americium solutions were dried, flamed, and counted in a low-geometry counter* of measured geometry known to 0·01 per cent. In the first ^{243}Am metal sample the amount of material was so small that after weighing the metal was dissolved directly on the counting plate in a drop of sulphuric acid containing about 1 λ of HCl. More than 10^6 counts were registered for each plate. An α-pulse analysis of each solution was made and no α-particles other than ^{241}Am alphas were found in that solution. The ^{243}Am solution was found to contain 99·35 per cent ^{243}Am α-particles, 0·50 per cent ^{241}Am α-particles, and 0·15 per cent ^{244}Cm α-particles.

The specific-activity determinations are summarized in Table 1. This value of 457·7 years for the half-life for ^{241}Am is to be compared with the value of $458{\cdot}1 \pm 0{\cdot}5$ years obtained by HALL and MARKIN[5] from extremely careful determinations of the specific-activity of $Am_2(SO_4)_3$ and $AmCl_3$. It should also be noted that the agreement between the metal and salt values indicates that no residue resulted from the dissolution of americium metal, unlike the situation with thorium, uranium, or plutonium. This is in accord with the lanthanum like properties of americium metal.[4] The uncertainty in the half-life of ^{241}Am is estimated to be 0·4 per cent (balance calibration 0·1 per cent, impurity content 0·15 per cent, counting 0·1 per cent aliquoting 0·07 per cent), yielding a half-life of $457{\cdot}7 \pm 1{\cdot}8$ years; the uncertainty in the half-life of ^{243}Am is estimated to be 0·6 per cent (balance calibration 0·1 per cent, impurity content 0·15 per cent, counting 0·1 per cent, aliquoting 0·17 per cent, pulse analysis 0·1 per cent), yielding a half-life of 7951 ± 48 years.

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* H. P. ROBINSON states that a description of this counter is to be published by the National Research Council, Subcommittee for Standards and Measurement of Radioactivity, in the proceedings of a conference held October 9–11, 1957 at Easton, Md.

[5] G. R. HALL and T. L. MARKIN, *J. Inorg. Nucl. Chem.* **4**, 137 (1957).

J. Inorg. Nucl. Chem., 1958, Vol. 7, pp. 201 to 209. Pergamon Press Ltd., London

ZUR KINETIK DER ELEKTROCHEMISCHEN ABSCHEIDUNG RADIOAKTIVER IONENARTEN AUF METALLOBERFLÄCHEN

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Abstract—The NERNST–BRUNNER equation has been applied to the electrochemical deposition of carrier-free radioactive ions on metal foils in a modified form to include decay and growth. The modified equation was shown to hold for the deposition of ^{212}Bi(ThC) and ^{210}Bi(RaE) on nickel foils from weak hydrochloric acid solutions under the following conditions: pure ^{212}Bi, ^{212}Bi in equilibrium with ^{212}Pb(ThB), ^{212}Bi in equilibrium with ^{228}Th(RdTh), and ^{210}Bi in equilibrium with ^{210}Pb(RaD). Some indications of the purity of the deposited radio-bismuth are given.

DIE elektrochemische Abscheidung trägerfreier Radioisotope ist eine in der Radiochemie viel verwendete präparative Methode. Schon 1902–03 führten MARCKWALD[1] und LERCH[2] diese Methode zur Isolierung von Gliedern der natürlichen Zerfallsreihen ein, während HAISSINSKY[3] sie kurz nach der Entdeckung der künstlichen Radioaktivität erstmals zur Abtrennung eines künstlichen Radioisotops verwendete.

Bei der Durchführung elektrochemischer Abscheidungen ist es wünschenswert, dass der Reaktionsablauf aus wenigen experimentellen Daten vorausberechnet werden kann. Reaktionen, die sich an der Grenzfläche zwischen Festkörpern und Lösungen abspielen, hat NERNST[4] theoretisch behandelt. Die von ihm abgeleitete Gleichung für die Reaktionsgeschwindigkeit basiert darauf, dass der Materietransport von der Lösung zum Festkörper oder umgekehrt durch Diffusion erfolgt. Geschwindigkeitsbestimmend ist die Diffusion durch eine dem Festkörper anhaftende dünne Flüssigkeitslamelle.

Den experimentellen Beweis für die Gültigkeit dieser Theorie erbrachte Nernsts Schüler BRUNNER.[5] Dass die Gleichung auch auf die galvanische Abscheidung anwendbar ist, zeigten CENTNERSZWEER und DRUCKER[6] für die Entladung von Kupferionen an Zink. Für die elektrochemische Abscheidung eines trägerfreien Radioisotops wurde die NERNST–BRUNNERsche Gleichung erstmals von TAMMANN und WILSON[7] sowie ERBACHER und PHILIPP[8] benutzt. Bei den erstgenannten Untersuchungen wurde mit langlebigen Radioisotopen gearbeitet, so dass die Abscheidung nicht durch den Zerfall der Aktivität während des Experimentes beeinflusst wurde.

* Diplomarbeit Mainz 1957.

(1) W. MARCKWALD, *Ber. dtsch. chem. Ges.* **35**, 2285 (1902).
(2) F. LERCH, *Ann. Phys., Lpz.* **12**, 758 (1903).
(3) M. HAISSINSKY, *Nature, Lond.* **136**, 141 (1936).
(4) W. NERNST, *Z. phys. Chem.* **47**, 52 (1904).
(5) E. BRUNNER, *Z. phys. Chem.* **47**, 56 (1904).
(6) M. CENTNERSZWEER und J. DRUCKER, *J. chim. phys.* **13**, 196 (1915).
(7) G. TAMMANN und C. WILSON, *Z. anorg. Chem.* **173**, 137 (1928).
(8) O. ERBACHER und K. PHILIPP, *Z. Phys.* **51**, 309 (1928).

Bei der Anwendung der NERNST–BRUNNERschen Gleichung auf kurzlebige Radioisotope muss dieser Zerfall berücksichtigt werden. Ebenso ist eine Abänderung der Gleichung notwendig, wenn die sich abscheidende Substanz laufend aus einer in der Lösung vorhandenen Muttersubstanz nachgeliefert wird. Beide Effekte—Zerfall und Nachbildung—werden in der in Abschnitt 1 abgeleiteten Gleichung berücksichtigt. Die erhaltene Gleichung wird in Abschnitt 2 mit experimentellen Daten verglichen.

1. ABSCHEIDUNGSGLEICHUNG FÜR RADIOISOTOPE

Folgende Bezeichnungen und Abkürzungen werden verwendet:

- t Dauer der Exposition
- a Zahl der Atome der sich abscheidenden Substanz bei Versuchsbeginn ($t = 0$)
- x Zahl der zur Zeit t insgesamt abgeschiedenen Atome
- z Zahl der Atome der sich abscheidenden Substanz in der Lösung zur Zeit t
- y Zahl der zur Zeit t auf dem Blech noch vorliegenden Atome
- n_M, N_M Zahl der Atome der Muttersubstanz der sich abscheidenden Substanz zur Zeit t bzw. $t = 0$
- λ_T Zerfallskonstante der sich abscheidenden Substanz
- λ_M Zerfallskonstante der Muttersubstanz der sich abscheidenden Substanz
- F geometrische Blechoberfläche
- V Volumen der Lösung
- D Diffusionskoeffizient der sich abscheidenden Substanz
- i Dicke der am Blech anhaftenden Flüssigkeitslamelle
- k Abscheidungskonstante, $k = D/i$

$r = D \cdot F/i \cdot V = k \cdot F/V$

Um während der Abscheidung Zerfall und Nachbildung zu berücksichtigen, geht man von folgenden Gleichungen aus:

$$\frac{dx}{dt} = r \cdot z \tag{1}$$

$$\frac{dz}{dt} = \lambda_M \cdot n_M - \lambda_T \cdot z - r \cdot z \tag{2}$$

$$\frac{dy}{dt} = \frac{dx}{dt} - \lambda_T \cdot y \tag{3}$$

Gleichung (1) ist der Differentialansatz der NERNST–BRUNNERschen Gleichung (8). Der Ansatz besagt, dass die Abscheidungsgeschwindigkeit dx/dt proportional der jeweils in der Lösung vorhandenen Atomzahl der sich abscheidenden Substanz ist.

Ist diese Substanz radioaktiv, so nimmt z nicht nur durch die Abscheidung, sondern auch durch den radioaktiven Zerfall ab. Andererseits wird die Substanz laufend aus einer Muttersubstanz nachgeliefert. Die zeitliche Änderung von z ist also durch die Abscheidungsgeschwindigkeit ($r \cdot z$), die Zerfallsgeschwindigkeit ($-\lambda_T \cdot z$) und die Nachbildungsgeschwindigkeit ($\lambda_M \cdot n_M$) gegeben—Gleichung (2).

Es ist jetzt noch der Zerfall der Substanz auf dem Blech zu berücksichtigen. Die dort zur Zeit t vorliegende Atomzahl y ändert sich durch die Nachlieferung aus der

Lösung, gegeben durch die Abscheidungsgeschwindigkeit (dx/dt), und den radioaktiven Zerfall, gegeben durch die Zerfallsgeschwindigkeit ($-\lambda_T \cdot y$)—Gleichung (3).

Gesucht wird eine Gleichung, die y in Abhängigkeit von t gibt. Dazu wird zunächst Gleichung (2) integriert. Berücksichtigt man, dass

$$n_M = N_M \cdot e^{-\lambda_M \cdot t}, \tag{a}$$

$$z = a \qquad \text{für} \qquad t = 0 \tag{b}$$

ist, so folgt:

$$z = \frac{\lambda_M \cdot N_M}{\lambda_T - \lambda_M + r} \cdot (e^{-\lambda_M \cdot t} - e^{-(\lambda_T + r) \cdot t}) + a \cdot e^{-(\lambda_T + r) \cdot t} \tag{2a}$$

Gleichung (2a) wird in (1) eingesetzt und (1) in Gleichung (3) eingesetzt. Es folgt:

$$\frac{dy}{dt} = -\lambda_T \cdot y + \frac{r \cdot \lambda_M \cdot N_M}{\lambda_T - \lambda_M + r} \cdot (e^{-\lambda_M \cdot t} - e^{-(\lambda_T + r) \cdot t}) + r \cdot a \cdot e^{-(\lambda_T + r) \cdot t} \tag{3a}$$

Die Integration dieser Gleichung (3a) liefert schliesslich mit $y = 0$ für $t = 0$ die allgemeine Lösung:

$$y = \frac{r \cdot \lambda_M \cdot N_M}{(\lambda_T - \lambda_M + r) \cdot (\lambda_T - \lambda_M)} \cdot e^{-\lambda_M \cdot t} - \left(a - \frac{\lambda_M \cdot N_M}{\lambda_T - \lambda_M + r}\right) \cdot e^{-(\lambda_T + r) \cdot t} + \\ + \left(a - \frac{\lambda_M \cdot N_M}{\lambda_T - \lambda_M + r} - \frac{r \cdot \lambda_M \cdot N_M}{(\lambda_T - \lambda_M + r) \cdot (\lambda_T - \lambda_M)}\right) \cdot e^{-\lambda_T \cdot t} \tag{4}$$

Diese Lösung gilt allgemein für jedes Verhältnis von Mutter- zu Tochtersubstanz; es braucht also zu Versuchsbeginn kein radioaktives Gleichgewicht vorzuliegen. Für den Fall des Gleichgewichtes vereinfacht sich die Abscheidungsgleichung (4).

Laufendes Gleichgewicht. Für diesen Fall ist a gegeben durch:

$$a = \frac{\lambda_M \cdot N_M}{\lambda_T - \lambda_M}$$

Setzt man diesen Ausdruck in Gleichung (4) ein, so folgt:

$$y = \frac{a \cdot r}{\lambda_T - \lambda_M + r} \cdot (e^{-\lambda_M \cdot t} - e^{-(\lambda_T + r) \cdot t}) \tag{5}$$

Diese Gleichung (5) gilt auch für eine Serie von radioaktiven Substanzen im Gleichgewicht. Für λ_M ist dann die Zerfallskonstante der langlebigsten Substanz einzusetzen, die den Zerfall der Gleichgewichtsaktivität bestimmt.

Stationäres Gleichgewicht. Es ist

$$a = \lambda_M \cdot N_M / \lambda_T,$$

d.h. λ_M kann gegenüber λ_T als Summand vernachlässigt werden. Man erhält:

$$y = \frac{a \cdot r}{\lambda_T + r} \cdot (e^{-\lambda_M \cdot t} - e^{-(\lambda_T + r) \cdot t}) \tag{6}$$

Substanz ohne Nachbildung. Wird die sich abscheidende Substanz rein angewendet und nicht aus einer Muttersubstanz laufend nachgeliefert, so ist in Gleichung (4) $N_M = 0$ zu setzen. Es resultiert:

$$y = a \cdot e^{-\lambda_T \cdot t} \cdot (1 - e^{-r \cdot t}) \tag{7}$$

Man erkennt die Analogie zur NERNST–BRUNNERschen Gleichung (8). Es tritt lediglich die Zerfallsfunktion hinzu.

NERNST–BRUNNER*sche Gleichung als Grenzfall.* Setzt man in Gleichung (7) $\lambda_T = 0$, d.h. ist die sich abscheidende Substanz nicht radioaktiv, so ergibt sich wieder die NERNST–BRUNNERsche Gleichung:

$$y = a \cdot (1 - e^{-r \cdot t}) \tag{8}$$

Die Gleichung (8) kann auch bei radioaktiven Substanzen angewendet werden, wenn während der Versuchsdauer keine merkliche Aktivitätsänderung durch Zerfall oder Nachbildung erfolgt.

Optimale Versuchsdauer. Eine Betrachtung der Gleichungen (5) und (7) zeigt, dass in diesen Fällen die Abscheidungskurve ein Maximum hat, welches sehr ausgeprägt sein kann, wenn die sich abscheidende Substanz—Gleichung (7)—oder die Muttersubstanz—Gleichung (5)—während des Versuches in beträchtlicher Menge zerfällt. Für diese Fälle ist es angebracht, die optimale Versuchsdauer t_{opt} zu berechnen, in der y den Höchstwert erreicht. Man findet t_{opt} durch $dy/dt = 0$ und erhält für den Fall des laufenden Gleichgewichtes:

$$t_{opt} = \frac{1}{\lambda_M - \lambda_T - r} \cdot \ln \frac{\lambda_M}{\lambda_T + r} \tag{5a}$$

und für den Fall, dass keine Nachbildung der sich abscheidenden Substanz erfolgt

$$t_{opt} = \frac{1}{r} \cdot \ln \frac{\lambda_T + r}{\lambda_T} \tag{7a}$$

2. EXPERIMENTELLE PRÜFUNG DER ABSCHEIDUNGSGLEICHUNG

Die im Abschnitt 1 abgeleiteten Gleichungen wurden durch die Messung der Abscheidungskurven von Radiowismut auf Nickelblechen aus siedender verdünnter Salzsäure geprüft. Dabei wurden die verschiedenen Formen der Abscheidungsgleichung auf folgende Systeme angewendet:

(a) Abscheidung eines kurzlebigen Radioisotops ohne Nachbildung—Gleichung (7): ^{212}Bi(ThC) aus ^{212}Bi(ThC)—Lösung.

(b) Abscheidung eines kurzlebigen Radioisotops im laufenden Gleichgewicht mit der Muttersubstanz—Gleichung (5): ^{212}Bi(ThC) aus ^{212}Pb(ThB)—Lösung.

(c) Abscheidung eines kurzlebigen Radioisotops im stationären Gleichgewicht mit der Muttersubstanz—Gleichung (6): ^{212}Bi(ThC) aus ^{228}Th(RdTh)—Lösung.

(d) Abscheidung eines langlebigen Radioisotops—Gleichung (8): ^{210}Bi(RaE) aus ^{210}Pb(RaD)—Lösung.

Die Halbwertszeiten der verwendeten Radioisotope betragen: ^{212}Bi 60,5 m, ^{212}Pb 10,6 h, ^{228}Th 1,9 a, ^{210}Bi 5,0 d, ^{210}Pb 22,3 a.

Methode. Die Abscheidung wurde aus siedender n/10 HCl in einem Becherglas vorgenommen, das mit einer Glasplatte verschlossen war. Zur Konstanthaltung des Volumens war ein Rückflusskühler angeschlossen. Die Nickelbleche wurden in einem Glasgestell untergebracht, das der Lösung ungehinderten Zutritt zur Blechoberfläche gestattete.

Die mit Methanol entfetteten Bleche wurden 20–30 sec mit siedender HNO_3 1 : 1 angeätzt, abgespült und in die bereits siedende Radiowismutlösung—Volumen 250 ml—gegeben. Um ein gleichmässiges Sieden zu erreichen, wurden Siedesteine zugesetzt. Nach der Exposition wurde das Blech in HNO_3 aufgelöst und nach Zugabe von Trägerwismut das ThC bzw. RaE als Bi_2S_3 aus der

warmen, 0,5 n sauren Lösung ausgefällt. Der Niederschlag wurde filtriert, mit einem Glockenzählrohr gemessen und die Aktivität auf das Versuchsende zurückextrapoliert.

Die gemessenen Aktivitäten wurden korrigiert, um das Auflösungsvermögen der Zählanordnung zu berücksichtigen. Weitere Korrekturen waren nicht notwendig, da die Präparatdicke, der Präparatdurchmesser, die Dicke der Unterlage und die Lage des Präparates zum Zählrohr in allen Fällen gleich gehalten wurden. Auch die Gehaltsbestimmung der für den Versuch verwendeten Lösungen erfolgte unter den gleichen Bedingungen. Zur Bestimmung der Wismutisotope in Gemischen wurden Absorptionsmessungen durchgeführt und nach HARLEY und HALLDEN[9] ausgewertet.

Nach dem Zerfall der Wismutisotope blieben vorliegende Verunreinigungen als langlebige Komponente zurück und konnten so identifiziert und bestimmt werden.

TABELLE 1.—BESTIMMUNG DER ABSCHEIDUNGSKONSTANTEN k

$F = 60$ cm²	$t =$ 10 min	$100x/a = 56$ %	$k = 0{,}35$ cm/min
	20	80	0,33
$F = 10$ cm²	$t =$ 62 min	$100x/a = 65$ %	$k = 0{,}43$ cm/min
	100	77	0,37
	120	85	0,41

Für die Versuche wurden käufliche trägerfreie Lösungen von RdTh und RaD benutzt. Trägerfreie ThB-Lösungen wurden aus Thoron durch Exposition eines Pt-Bleches über einem RdTh-haltigen Eisenhydroxydpräparat gewonnen. Trägerfreie ThC-Lösungen wurden nach einem von GLEU[10] angegebenen Verfahren hergestellt: RdTh wird auf einem Kationenaustauscher adsorbiert und das ThC mit 0,5 n HCl eluiert.

Bestimmung der Abscheidungskonstanten k. Zur Berechnung der Abscheidungskurven aus den in Abschnitt 2 gegebenen Gleichungen benötigt man die für die Abscheidung massgebliche Grösse $r = D \cdot F/i \cdot V$. Während F, die geometrische Blechoberfläche, und V, das Volumen der Lösung, durch die Versuchsbedingungen bekannt sind, sind der Diffusionskoeffizient D und die Dicke der am Blech anhaftenden Flüssigkeitslamelle i im allgemeinen unbekannt. Nach NERNST[4] fasst man beide Grössen zur Abscheidungskonstanten $k = D/i$ zusammen. k muss durch einige Versuche unter möglichst einfachen Versuchsbedingungen bestimmt werden. Wir wählten dazu die Abscheidung von ^{210}Bi(RaE) aus ^{210}Pb(RaD)-Lösung, weil in diesem Fall während des Versuchs kein merklicher Zerfall oder Nachbildung des RaE erfolgt. Es kann dann die NERNST–BRUNNERsche Gleichung (8) benutzt werden. k ergibt sich zu:

$$k = \frac{V}{F \cdot t} \cdot \ln \frac{a}{a - x} \tag{9}$$

Die zur Bestimmung von k durchgeführten Versuche sind in Tabelle 1 zusammengestellt. Im Mittel ergab sich: $k = 0{,}38 \pm 0{,}05$ cm/min.

Vergleich der gefundenen und berechneten Abscheidungskurven. Mit dem nach Tabelle 1 erhaltenen Wert für k wurden die Abscheidungskurven berechnet. Die Kurven sind in den Abb. 1–4 wiedergegeben. Dort ist angegeben, wieviel % der bei Versuchsbeginn vorliegenden Aktivität bei Versuchsende abgeschieden sind, d.h. 100 y/a. Die Übertragung der in den Gleichungen eigentlich berechneten Atomzahlen auf Aktivitäten ist möglich, da die Aktivität der Zahl der vorliegenden Atome

[9] J. HARLEY und N. HALLDEN, *Nucleonics* **13**, No. 1, 32 (1955).
[10] K. GLEU, K. H. KÖNIG und H. WAGNER, *Z. anorg. Chem.* **290**, 270 (1957).

proportional ist. In den Abbildungen sind gleichzeitig auch die experimentellen Werte eingetragen. Der mittlere Fehler der Messwerte liegt bei etwa 10%.

Es zeigt sich, dass die berechneten Kurven mit den experimentellen Daten befriedigend übereinstimmen. Systematische Abweichungen sind allerdings nicht zu übersehen. So ist bei kleinen Blechoberflächen die gemessene Abscheidungsquote anfangs grösser als die berechnete. Durch eine Vergrösserung der Abscheidungskonstanten kann man erreichen, dass bei kleiner Expositionsdauer die berechnete und gefundene

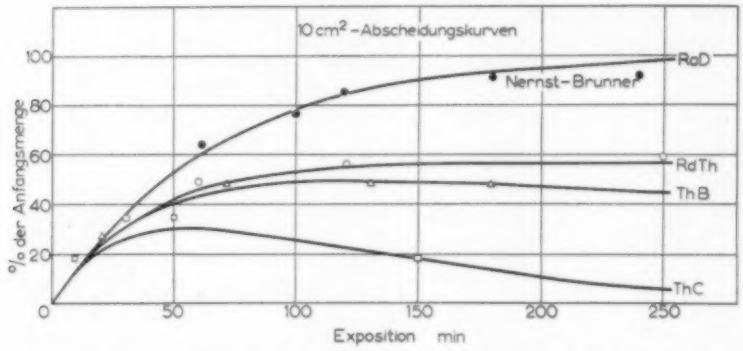

ABB. 1.—Abscheidungskurven für ThC aus reiner ThC-Lösung (□), aus ThB-Lösung (△), aus RdTh-Lösung (○) und für RaE aus RaD-Lösung (●), 10 cm² Nickelblech. Die ausgezogenen Kurven sind nach den Gleichungen (7), (5), (6) und (8) berechnet.

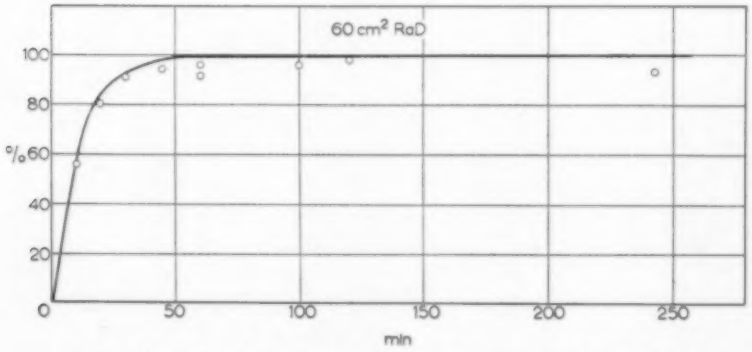

ABB. 2.—Abscheidungskurve für RaE aus RaD-Lösung, 60 cm² Nickelblech. Die ausgezogene Kurve ist nach Gleichung (8) berechnet.

Abscheidungsquote identisch werden; dann werden jedoch die Differenzen bei grosser Expositionsdauer noch grösser.

Diffusionsschichtdicke. Aus $k = D/i$ kann man i abschätzen, wenn D bekannt ist. VON HEVESY[11] hat den Diffusionskoeffizienten des RaE in n/100 HCl bei 18°C zu $D = 0{,}65$ cm²/Tag gemessen. Daraus ergibt sich nach NERNST[12] bei 100°C ein Diffusionskoeffizient von

$$D_{100} = D_{18} \cdot (1 + 0{,}026 \cdot (100 - 18)) = 1{,}4 \cdot 10^{-3} \text{ cm}^2/\text{min}.$$

[11] G. VON HEVESY, *Phys. Z.* **14**, 56 (1913).
[12] W. NERNST, *Z. phys. Chem.* **2**, 24 (1888).

Mit $k = 0{,}38$ cm/min erhält man $i = 4 \cdot 10^{-3}$ cm, während NERNST und BRUNNER[5] Werte zwischen $2 \cdot 10^{-3}$ bis $5 \cdot 10^{-3}$ cm für andere heterogene Vorgänge erhielten. TAMMANN und WILSON[7] fanden $6 \cdot 10^{-3}$ cm und ERBACHER und PHILLIPP[8] $1 \cdot 10^{-3}$

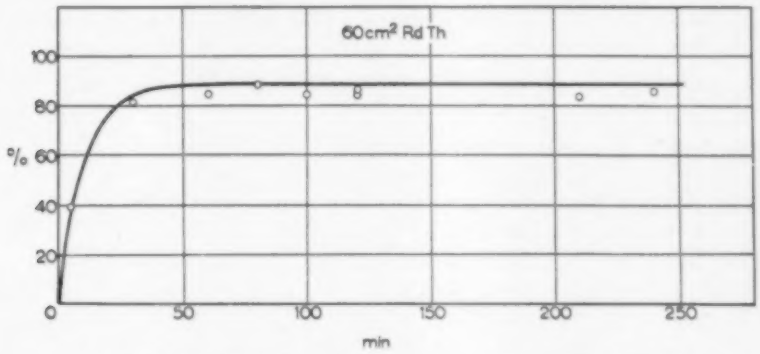

ABB. 3.—Abscheidungskurve für ThC aus RdTh-Lösung, 60 cm² Nickelblech. Die ausgezogene Kurve ist nach Gleichung (6) berechnet.

cm für elektrochemische Abscheidungen, allerdings unter anderen Versuchsbedingungen.

3. DISKUSSION

Die Untersuchung zeigt, dass die NERNST–BRUNNERsche Gleichung auch auf die Abscheidung trägerfreier Radioisotope anwendbar ist, wenn Zerfall und Nachbildung berücksichtigt werden. Durch Bestimmung oder Schätzung der Abscheidungskonstanten k kann der Verlauf der Abscheidungskurve festgelegt werden.

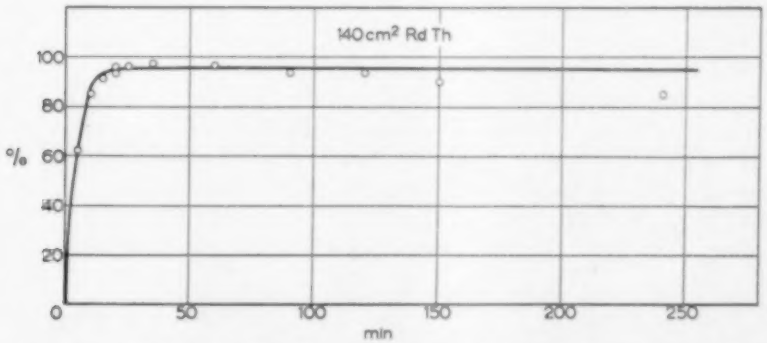

ABB. 4.—Abscheidungskurve für ThC aus RdTh-Lösung, 140 cm² Niblech. Die ausgezogene Kurve ist nach Gleichung (6) berechnet.

Die Abweichungen vom berechneten Kurvenverlauf werden für die Anwendung der Gleichung in der Regel unerheblich sein. Ihre Ursachen können zur Zeit nur vermutet werden. Der Effekt ist besonders auffällig in Abb. 1—Blechoberfläche 10 cm². Eine Bestimmung der auf der Blechoberfläche vorliegenden Menge an inaktivem Wismut durch Verdampfung im Wasserstoffstrom und anschliessende

spektrochemische Analyse[13] ergab eine Belegung von 0,5 cm² des Bleches durch inaktives Wismut. Das bedeutet, dass die Blechoberfläche, die für die Abscheidungsgeschwindigkeit mit massgebend ist, während des Versuches kleiner wird. ERBACHER[14] fand, dass die Abscheidung von ThC auf Nickel aufhört, wenn die Oberfläche des Nickels mit Wismutatomen vollständig belegt ist. Auch durch die Einwirkung der Säure auf das Nickelblech sind Oberflächenänderungen wahrscheinlich. Man wird dabei annehmen dürfen, dass mit dem Nickel auch ein Teil des abgeschiedenen Wismuts rückgelöst wird.

Die gefundene Dicke der Diffusionsschicht i stimmt mit den Werten anderer Autoren überein, wenn man berücksichtigt, dass i stark von den Versuchsbedingungen —Temperatur, Durchmischung der Lösung—abhängt. Es ist allerdings fraglich, ob die i-Werte der wahren Schichtdicke entsprechen. i wird aus der empirischen Konstanten k errechnet; k wird aus Gleichung (9) gewonnen, in welcher die geometrische Blechoberfläche F eingesetzt wird. Es ist anzunehmen, dass statt der geometrischen die wahre, kristalline Oberfläche des Bleches für die Abscheidung massgebend ist. In k ist dann ein entsprechender Proportionalitätsfaktor enthalten, der zugleich auch das Verhältnis der gefundenen Diffusionsschichtdicke i zur wahren Dicke wiedergibt. TAMMANN und WILSON[7] haben z.B. gefunden, dass k von der Vorbehandlung des zur Abscheidung benutzten Bleches abhängt, ein Einfluss, den man auf eine verschiedenartige wahre Oberfläche zurückführen kann.

In der Konstanten k dürften noch weitere Faktoren enthalten sein, die die Abscheidung mehr oder weniger stark beeinflussen.

Gültigkeitseinschränkung der Abscheidungsgleichung. Da bei der Ableitung der Gleichungen Zerfall und Nachbildung innerhalb der Diffusionsschicht nicht berücksichtigt sind, darf innerhalb der Diffusionsdauer keine merkliche Nachbildung und kein Zerfall erfolgen. Es gilt für makromolekulare Teilchen:[15] $D = i^2/2t_d$. Darin ist i der Diffusionsweg, also die Dicke der Diffusionsschicht, und t_d ist die mittlere Diffusionsdauer zur Zurücklegung des Weges i.

Setzt man nach NERNST[4] $D = k \cdot i$, so folgt: $t_d \approx 1$ sec. Damit ergibt sich, dass die Halbwertszeit der sich abscheidenden Substanz grösser als etwa 1 min sein muss, wenn der durch die oben erwähnte Vernachlässigung bedingte Fehler innerhalb der bei diesen Versuchen auftretenden Fehlergrenzen bleiben soll. Andererseits ist bei Substanzen, deren Halbwertszeit kleiner als 1 min ist, die Ausbeute bei der Abscheidung so gering, dass sich die präparative Anwendung der elektrochemischen Abscheidung im allgemeinen nicht lohnt.

4. REINHEIT

An Verunreinigungen wurden im aus trägerfreien Lösungen abgeschiedenen ThC circa 0,01% des vorhandenen ThB(^{212}Pb) pro 10 cm² Blechoberfläche gefunden. Die Verunreinigung durch RdTh(^{228}Th) betrug bis zu 25% des vorhandenen RdTh bei 140 cm² Blechoberfläche. Es dürfte sich um eine Abscheidung von Thoriumhydroxyd handeln, das in der Nähe der Bleche durch Hydrolyse, bedingt durch die Verarmung an H^+-Ionen, entsteht.

Versuche zur Abscheidung von ThC aus wägbaren Mengen Thoriumsalzen (25 g Th-Salz/250 ml) zeigten, dass die Abscheidung aus Thoriumnitratlösung durch

[13] A. SPANG, Dissert. Mainz 1957. Wir danken Herrn DR. SPANG für die Durchführung der Analyse.
[14] O. ERBACHER, *Z. phys. Chem.* **A 163**, 215 (1933).
[15] cit. A. EUCKEN, *Lehrb. chem. Phys.* **II**, 1062 (1949).

die Hydrolyse des Thoriums sehr gestört wird. Durch die Verwendung von Thoriumchloridlösung wurde diese Schwierigkeit behoben. Es wurden brauchbare Ausbeuten an ThC erzielt, die allerdings stärker schwankten als bei der Anwendung trägerfreier Lösungen.

Herrn Diplomphysiker G. BIMSCHAS danken wir sehr für seine wertvolle Mitarbeit bei der Ableitung der Abscheidungsgleichung.

Der DEUTSCHEN FORSCHUNGSGEMEINSCHAFT und dem BUNDESMINISTERIUM FÜR ATOMKERNENERGIE UND WASSERWIRTSCHAFT sind wir für finanzielle Unterstützung zu Dank verpflichtet.

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THE CHEMICAL EFFECT OF ALPHA PARTICLES ON URANIUM HEXAFLUORIDE*

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Abstract—Alpha-particle decomposition of uranium hexafluoride has been studied over the temperature range 26° to 87°C. Radiation was obtained by use of charges of about 0·1 c Rn-222. Products of the decomposition are fluorine and intermediate uranium fluorides; the products react with each other, apparently by a radiation-induced process, to re-form uranium hexafluoride. Reaction rates are independent of temperature over the temperature range studied. Average values of G_U and M/n are, respectively, 0·90 and 0·27, the latter being based on loss of 30 eV by an α-particle when it produces one ion pair.

ALTHOUGH a great many reactions initiated by α-particle radiation have been studied,[1] apparently no such reactions involving uranium compounds have been investigated. The latter are of particular interest because of the fact that uranium is itself an α-particle emitter, and, thus, all of its compounds are continuously subject to self-irradiation.

Normal uranium has a very weak α-intensity, the decay constant of ^{238}U being $4{\cdot}87 \times 10^{-18}$/sec.[2] The isotopes ^{235}U and ^{234}U, however, have larger constants, these being $3{\cdot}09 \times 10^{-17}$ and $8{\cdot}8 \times 10^{-14}$/sec, respectively. Nevertheless, the relative abundances of these isotopes in normal uranium are so small that, even taking into account their larger decay constants, normal uranium emits only about 25 α-particles/mg sec. Self-irradiation would, therefore, not produce any large chemical effects in normal uranium compounds. However, uranium which has been enriched 100-fold in ^{235}U and ^{234}U emits about 1230 α-particles/mg sec, roughly fifty times the number from normal uranium. A single α-particle from ^{234}U produces approximately $1{\cdot}37 \times 10^5$ ion pairs over its entire path. Thus, 1 g of uranium enriched 100-fold will produce about $5{\cdot}3 \times 10^{18}$ ion pairs per year. Assuming all α-particles are able to complete their paths within the uranium compound, about 0·2 per cent of the molecules present would have become ionized in the course of a year by self-α-irradiation, and the amount of chemical reaction as a result of this over any extended period of time might become quite appreciable.

Decomposition due to self-α-irradiation has recently been reported in three papers for plutonium hexafluoride.[3] Compounds of plutonium provide a much more

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[1] S. C. LIND, *The Chemical Effects of Alpha Particles and Electrons*. American Chemical Society Monograph Series, No. 2, revised edition, Reinhold, New York (1928).

[2] *Nucl. Sci. Abstr.* **9**, No. 21B, 123 (1955).

[3] C. J. MANDLEBERG, H. K. RAE, R. HURST, G. LONG, D. DAVIES and K. E. FRANCIS, *J. Inorg. Nucl. Chem.* **2**, 358 (1956); A. E. FLORIN, I. R. TANNENBAUM and J. F. LEMONS, *Ibid.* **2**, 368 (1956); B. WEINSTOCK and J. G. MALM, *Ibid.* **2**, 380 (1956).

striking example of this effect than would be expected of uranium compounds, since the disintegration rates of ^{239}Pu and ^{240}Pu are 2000–8000 times as great as uranium enriched 100 times in ^{234}U. Thus, reported values of plutonium hexafluoride decomposition by self-α-irradiation are in the order 1–2 per cent per day instead of a potential 0·2 per cent, or less, per year, for uranium compounds so enriched in ^{234}U.

The present study is concerned with the radiation chemistry of uranium hexafluoride under α-particle bombardment, since, in addition to the importance of its reactions on purely theoretical grounds, this compound is used in the gaseous diffusion process; any reactions it undergoes as it becomes enriched and while in storage become of practical significance.

EXPERIMENTAL

Apparatus

The reaction chamber in most of the experiments was constructed of a nickel cylinder connected by means of small-bore nickel tubing to a Booth–Cromer nickel-diaphragm pressure transmitter.[4] The transmitter chamber had an i.d. of 3 in. and a depth of 0·01 in. giving it a volume of approximately 1·2 cm^3. The volume of the connecting tubing was about 0·5 cm^3; total volume varied from about 7 to 36 cm^3.

It is desirable to have the ratio of the total volume to the volume of Booth–Cromer transmitter and the connecting tubing as large as possible so as to reduce the magnitude of the errors of temperature correction. However, large volumes are undesirable with gas reactions in which the total amount of reaction is small, as these proved to be.

In a few of the early experiments the reaction chamber was a Pyrex glass bulb connected by a Kovar seal to the pressure transmitter. Fig. 1 shows the arrangement of the various components of a reactor used in several of these experiments.

Materials

Radon used for the source of α-particles was obtained from 230 mg of radium on loan from the Bureau of Mines. The gas was collected and purified in a system previously described.[5]

Uranium hexafluoride contained less than 0·015 weight per cent impurity; further purification was accomplished by pumping the hexafluoride while it was maintained at −78°C. Fluorine was taken from standard fluorine cells,[6] and had an estimated purity greater than 95 per cent.

A lead box with 3 in. thick walls was used as a shield against the γ-radiation emitted from the reaction systems. Within this box was contained a second box constructed of ½ in. asbestos board. Heaters and a thermal regulator in this air thermostat permitted heating a reactor and maintaining its temperature constant to ±3°C.

Procedure

In preparing the system for an experimental run, the apparatus described above was pumped, flamed, and the zero point of the Booth–Cromer transmitter then determined. The system was purged a number of times with fluorine and again

[4] S. Cromer, *The Electronic Pressure Transmitter and Self Balancing Relay*. Sam Laboratories, Columbia University, MDDC-803 20 June (1944); declassified 20 March (1947).
[5] C. H. Shiflett, M. E. Steidlitz and W. Davis, Jr., *Rev. Sci. Instrum.* **21**, 842 (1950).
[6] J. Dykstra, S. Katz *et al.*, *Industr. Engng. Chem.* **47**, 883 (1955).

pumped and flamed. Finally, fluorine was admitted at just under atmospheric pressure and the system maintained at 80–100°C for at least 24 hr in order to fluorinate the metal surfaces. When the temperature at which a decomposition experiment was to be run exceeded 45°C, the time of fluorination was increased to several days.

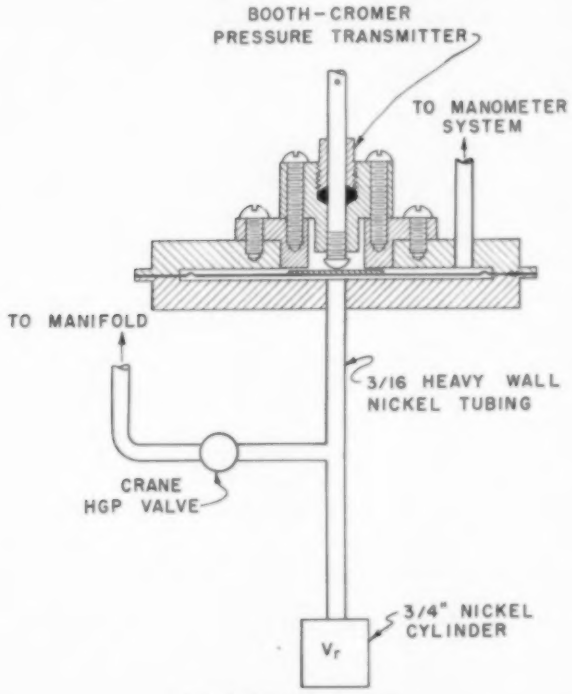

FIG. 1.—Reaction system.

Radon was admitted to the evacuated reactor by direct transfer from the radon purification plant.[5] The reactor was then connected to a manifold through which the various gases to be studied were admitted. After the experiment had proceeded for a few hours and the rate of pressure change well established manometrically, the reactor was immersed in a water-ice (0°C) or a dry-ice (−78°C) bath. These were contained in Dewar flasks which could be elevated through a door in the bottom of the thermostated box. Pressures at the lower temperatures were observed until thermal equilibrium had been attained. The low-temperature bath was then removed and the reaction allowed to proceed at the experimental temperature.

Randon charges used in the individual experiments were measured by γ-ray comparison with radium standards on loan from the Bureau of Mines. A Lind electrometer was used for the measurements.

RESULTS

Pressures of fluorine and uranium hexafluoride recorded in the figures of this report were obtained by correcting observed pressures to their equivalents at 0°C. These corrections were made by use of the ideal gas laws and may be summarized as

follows. Let total pressures measured at a reaction temperature T and at a lower temperature, say 0°C, be P_T and P_0, and the values corrected to 0°C be P°_T and P°_0. The conversion from P_0 to P°_0 includes a correction for that portion of the reactor volume (mainly the pressure transmitter) that is not immersed in the 0°C (low-temperature) bath. It has been assumed that uranium hexafluoride exhibits its vapour-pressure[7] of 17·3 mm at 0°C in the presence of fluorine. Thus, $P_0^\circ - 17{\cdot}3 = P^\circ_{F_2}$ is the pressure of fluorine in the system, corrected to 0°C; $P^\circ_T - P^\circ_{F_2} = P^\circ_{UF_6}$ is, by difference, the pressure of uranium hexafluoride, also corrected to 0°C.

TABLE 1.—RATIO OF FLUORINE PRESSURE INCREASE TO URANIUM HEXAFLUORIDE PRESSURE DECREASE

Expt. no.	$\lvert\Delta P_{F_2}/\Delta P_{UF_6}\rvert$
3	0·625
4	0·585
7	0·29
16	0·86
15	0·77
5	0·24
24	1·25

Under α-particle irradiation there is a depletion of uranium hexafluoride from the gas phase accompanied by an evolution of fluorine. Fig. 2 contains a summary of three typical experiments performed in a vessel originally containing no uranium fluoride deposit.

On addition of fluorine to uranium hexafluoride in a reactor containing solid uranium fluorides deposited from the gas phase, there is an initial increase followed by a decrease in the uranium hexafluoride pressure, as seen in Fig. 3.

TABLE 2.—RATIO OF FLUORINE PRESSURE INCREASE TO URANIUM HEXAFLUORIDE PRESSURE DECREASE FOR KNOWN URANIUM FLUORIDES

Compound	$\lvert\Delta P_{F_2}/\Delta P_{UF_6}\rvert$
UF_6	0·0
UF_5	0·5
UF_4	1·0
UF_3	1·5

It has not been possible to establish the exact identity of the solid uranium fluoride product, although some information is obtained from the ratio of fluorine produced to uranium hexafluoride decomposed. Such ratios for seven experiments are summarized in Table 1.

Ratios that would be obtained for several possible uranium fluoride products are listed in Table 2. In the presence of solid fluorides and added fluorine, the change in

[7] G. D. OLIVER, H. T. MILTON and J. W. GRISARD, *J. Amer. Chem. Soc.* **75**, 2827 (1953).

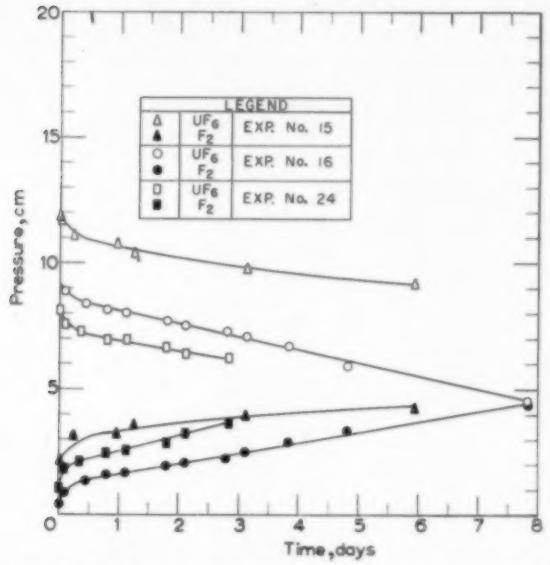

FIG. 2.—Time variation of UF_6 and F_2 pressures, corrected to 0°C.

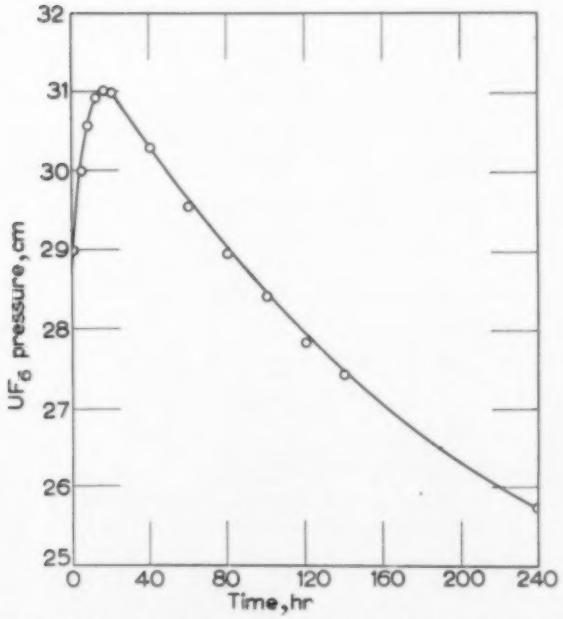

FIG. 3.—Time variation of UF_6 pressure, corrected to 0°C. Experiment 9, vessel initially contained UF_6 deposit.

fluorine pressure with uranium hexafluoride decomposition exhibits different values before and after the time of maximum uranium hexafluoride pressure, Fig. 3. These values are illustrated in Table 3.

TABLE 3.—COMPARISON OF THE CHANGE IN FLUORINE PRESSURE TO THE CHANGE IN URANIUM HEXAFLUORIDE PRESSURE IN THE PRESENCE OF THE SOLID FLUORIDES

Expt. no.	$\lvert\Delta P_{F_2}/\Delta P_{UF_6}\rvert$	
	Before max. UF_6 press	After max. UF_6 press
8	0·88 (F_2 depleted)	0·13 (F_2 formed)
9	0·67 (F_2 depleted)	0·28 (F_2 formed)

DISCUSSION

From the data obtained, it is obvious that the uranium hexafluoride is ionized by α-particles and dissociated to produce solid uranium fluorides. Chemical analyses have failed to aid in the identification of this material because the quantities available are so small (1–2 mg). X-ray diffraction patterns of the compound are not very clear due to the radiation background level and to small particle size, estimated to be less than 100 Å. However, halos have appeared in the region where β-uranium pentafluoride exhibits strong lines.[8] Such evidence is indicative but certainly not conclusive of the presence of some pentafluoride. As shown by the ratios of fluorine pressure change to uranium hexafluoride pressure change (Tables 1, 2 and 3), the solid compound may have a composition intermediate between uranium tetrafluoride and hexafluoride. Because further identification is not possible, the solid products are designated below as UF_x.

If the reaction of uranium hexafluoride under α-particle irradiation were to be dependent on the gas pressure and the radiation intensity alone, equation (1) could be used to represent the whole course of the decomposition.

$$UF_6 \xrightarrow{\alpha} UF_x + \left(\frac{6-x}{2}\right) F_2 \qquad \text{Rate constant} = k_1 \qquad (1)$$

The rate expression corresponding to equation (1) is

$$-\frac{d(UF_6)}{dt} = k_1(UF_6)E_0\,e^{-\lambda t}, \qquad (2)$$

where E_0 is the initial radon intensity, in curies, and λ is the decay constant of radon. This equation may then be integrated and solved according to equation (3), where $E/E_0 = e^{-\lambda t}$.

$$\log(UF_6) = \frac{k_1 E_0}{2{\cdot}303\lambda}\,e^{-\lambda t} + C \qquad (3)$$

If $\log(UF_6)$ or $\log P_{UF_6}$ is plotted against $\exp(-\lambda t) = E/E_0$, and the reaction is a simple decomposition, the data should follow a straight line with an intercept of C

[8] W. H. ZACHARIASEN, *Acta Cryst.* **2**, 296 (1949).

equal to $\log (UF_6)_0$ or $\log (P_{UF_6})_0$. Fig. 4 shows that this plot is not a straight line, but a curve of decreasing slope.

In view of the decreasing slope, a back reaction of the solid product with fluorine has been assumed. This reaction has been indicated to be dependent upon radiation, since, at the reaction temperatures employed, it is doubtful that measurable thermal

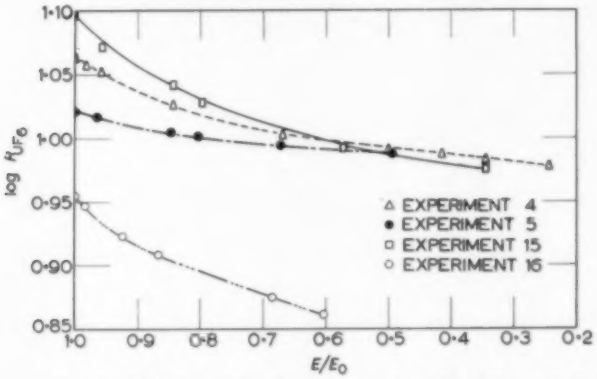

FIG. 4.—Variation of log P_{UF_6}, corrected to 0°C, with α-activity.

reaction would occur.[9] Further, when fluorine was placed and maintained at room temperature in a vessel that had previously been used in a radiation experiment, uranium hexafluoride was not formed in measurable quantities.

$$UF_x + \frac{(6-x)}{2} F_2 \xrightarrow{\alpha} UF_6 \qquad \text{Rate constant} = k_2 \tag{4}$$

The rate equation for the overall reaction of equations (1) and (4) may be written as

$$-\frac{d(UF_6)}{dt} = k_1 E_0 (UF_6) e^{-\lambda t} - k_2 E_0 (F_2)(S) e^{-\lambda t}, \tag{5}$$

where (S) is some function of the surface of solid UF_x. The fluorine concentration has been found experimentally to be a linear function of the uranium hexafluoride pressure, which is expressed by equation (6):

$$(F_2) = a - b(UF_6) \tag{6}$$

Typical correlations indicated by equation (6) may be seen in Fig. 5. Values of the constant b have been summarized in Tables 1 and 3. The rate equation may be rewritten following substitution of equation (6) into (5).

$$-\frac{d(UF_6)}{dt} = [\{k_1 + k_2(S)b\}(UF_6) - k_2(S)a] E_0 e^{-\lambda t} \tag{7}$$

Integration of equation (7) leads to the following relationship:

$$\ln \left[(UF_6) - \frac{k_2(S)a}{k_1 + k_2(S)b} \right] = \{k_1 + k_2(S)b\} \frac{E_0}{\lambda} e^{-\lambda t} + C \tag{8}$$

When values of k_1 and $k_2(S)$ are determined and the results plotted according to Fig. 6,

[9] J. J. KATZ and E. RABINOWITCH, *The Chemistry of Uranium*. Part I, NNES, MPTS, Div. VIII, Vol. 5, McGraw-Hill, New York (1951).

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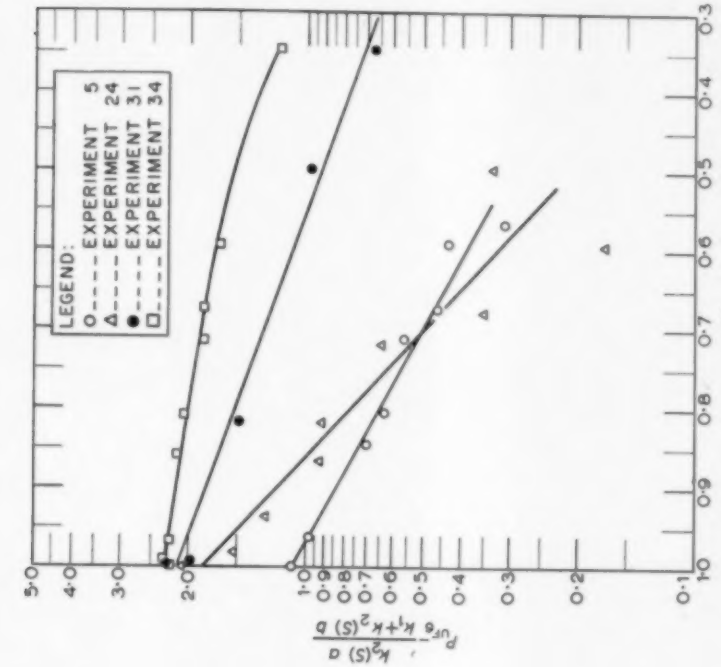

FIG. 6.—Correlation of experimental data according to equation (8).

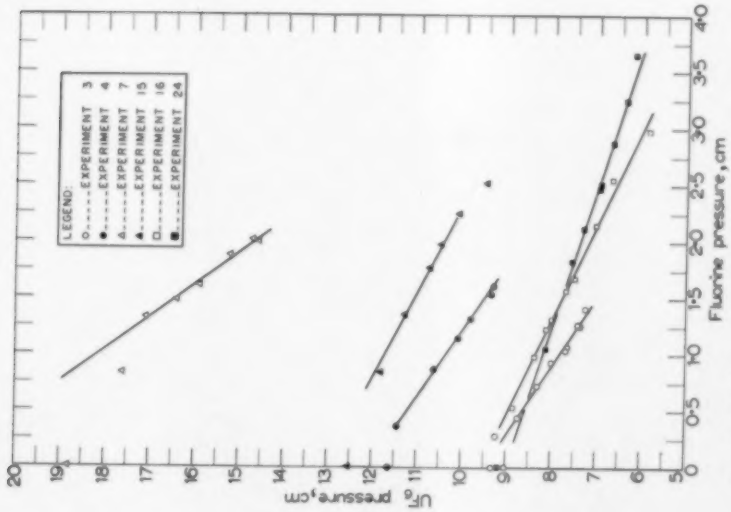

FIG. 5.—Variation of F_2 pressure with UF_6 pressure, corrected to 0°C.

a straight line results. Calculated values of k_1 and $k_2(S)$, determined by least-squares procedures, are listed in Table 4.

TABLE 4.—RATE CONSTANTS FOR URANIUM HEXAFLUORIDE DECOMPOSITION

Expt. no.	Temp. (°C)	Radon charge (c)	Initial UF_6 press* (mm Hg)	UF_6 decomposition $k_1 \times 10^5$ (c^{-1} sec^{-1})	UF_6 formation $k_2(S) \times 10^5$ (c^{-1} sec^{-1})
3†,‡	30	(0·1)	120	(3·95)	(23·05)
4†,‡	30	(0·1)	123	(2·04)	(13·49)
5‡	30	0·042	105	1·06	23·08
24	26	0·078	78·0	4·15	6·83
16	30	0·105	90·5	2·68	9·09
15	33	0·099	125·0	3·26	11·37
7	48	0·042	185·0	3·02	16·13
31	52	0·091	51·5	2·10	1·59
33	84	0·112	62·7	4·03	3·11
36	85	0·036	71·8	2·08	1·43
34	87	0·034	70·0	1·64	3·70

* Corrected to 0°C.
† The radon charge was not measured. The activity was estimated to be 100 mc.
‡ Experiments 3, 4, and 5 were carried out in spherical glass bulbs of radii 1·94, 1·96 and 1·98 cm, respectively.

Calculation of E_a, G, and M/n

Uranium hexafluoride can be ionized and decomposed to non-volatile uranium fluorides. These ionization processes are readily observable in a mass spectrometer; appearance potentials of the various ions, UF_5^+, UF_4^+, etc., have been reported by CAMERON.[10] The extent of a second decomposition process, namely electronic excitation of uranium hexafluoride molecules and their subsequent decomposition to free radicals (such as UF_5 and F) or molecules (such as UF_4 and F_2), is unknown. Since the relative importance of ionization and electronic excitation is not known, the quantity M/n, the number of molecules of uranium hexafluoride decomposed per ion pair, can be calculated but with more uncertainty than the quantity G, the number of molecules of uranium hexafluoride decomposed per 100 eV of energy absorbed. The latter term is independent of the mechanism of dissociation.

Terms used in calculating G, dN/dt, the number of molecules of uranium hexafluoride decomposed per sec, and dE_a/dt, the quantity of energy absorbed per sec (in eV/sec), are as follows.

e_1, e_2, e_3 = energies of α-particles from ^{222}Rn, ^{218}Po, and ^{214}Po, 5·486, 5·998 and 7·680 MeV, respectively;

e = average α-particle energy, $(e_1 + e_2 + e_3)/3 = 6{\cdot}388$ MeV;

S_1, S_2, S_3 = stopping powers of uranium hexafluoride for the ^{222}Rn, ^{218}Po, and ^{214}Po α-particles, respectively, cm^{-1} at *STP*;

S = average stopping power, $(S_1 + S_2 + S_3)/3$;

[10] A. E. CAMERON, *Determination of the Isotopic Composition of Uranium*. Technical Information Service, Oak Ridge, Tenn.; January, 1950; declassified February 1955 (TID-5213).

R_1, R_2, R_3 = ranges of ^{222}Rn, ^{218}Po, and ^{214}Po α-particles in uranium hexafluoride, cm at *STP*;
R = average α-particle range, $(R_1 + R_2 + R_3)/3$;
B = the number of α-particles emitted in 1 sec from a system containing 1 c of ^{222}Rn in equilibrium with its decay products, $3 \times 3{\cdot}72 \times 10^{10}$ α/sec c;
IP = the average amount of energy required to produce one ion pair, eV;

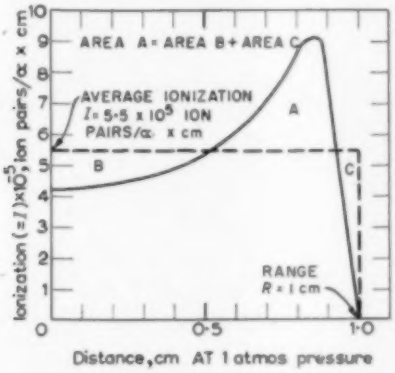

FIG. 7.—Schematic ionization curve.

L_1 = average path of an α-particle emitted from gaseous ^{222}Rn that is homogeneously distributed in a sphere of internal radius r;
$L_2 = L_3$ = average path of an α-particle emitted from solid ^{218}Po or solid ^{214}Po that is uniformly distributed on the inner surface of a sphere of internal radius r;
A = Loschimdt number, $2{\cdot}69 \times 10^{19}$ molecules/cm^3 at *STP*;
λ = decay constant of ^{222}Rn, $2{\cdot}10 \times 10^{-6}$/sec;
n_i = number of α-particles per sec from nucleus i(i = ^{222}Rn, ^{218}Po, ^{214}Po);
P_j = pressure of gas j, atm;
V_r = principal volume of reactor (Fig. 1), cm^3;
V_s = total reactor volume, cm^3

LIND[1] has shown that the average paths of α-particles are related to the radius, r, of a spherical container by equation (9).

$$L_1 = 0{\cdot}75r$$
$$L_2 = L_3 = 0{\cdot}5r \tag{9}$$

An accurate calculation of the rate of absorption of energy by a mixture of gases in a spherical container of volume V, radius r, at pressure P, containing initially E_0 c of radon can be made only if the ionization curve of each α-particle from the radon decay scheme in each pure gas is known. Such ionization curves, schematically shown in Fig. 7, have not been measured for uranium hexafluoride. Thus, estimates of G are based on an estimate of the average range, R, of the radon scheme α-particles in this gas, or on the number of ion pairs produced per cm of α-particle path.

If the only assumption involved in calculating the energy absorption rate, dE_a/dt,

were that ionization be constant over the path, then equation (10) could be written if the path length is less than the range (i.e. every α-particle reaches the wall).

$$\frac{d(E_a)_{ij}}{dt} = \frac{L_{ij}}{R_{ij}} e_i P_j n_i \tag{10}$$

Subscript i refers to the α-particle, j to the gas. The quantity n_i may be expressed as

$$n_i = \frac{B}{3} E_0 e^{-\mu}. \tag{11}$$

Then

$$\frac{dE_a}{dt} = \frac{B}{3} E_0 e^{-\mu} \sum_{i,j} \frac{L_{ij}}{R_{ij}} e_i P_j \tag{12}$$

or

$$\frac{dE_a}{dt} = \frac{B}{3} E_0 e^{-\mu} \sum_j \left\{ \frac{0{\cdot}75\, r}{R_{1j}} e_1 + 0{\cdot}5\, r \left(\frac{e_2}{R_{2j}} + \frac{e_3}{R_{3j}} \right) \right\} P_j \tag{13}$$

Quantities R_{ij} have not been determined experimentally, but have been calculated as described below. The necessity of estimating R makes the use of specific values of e_i superfluous; hence, e_i has been replaced by the average value e in equation (14).

$$\frac{dE_a}{dt} = \frac{BeE_0 e^{-\mu}}{3} r \sum_j \frac{1{\cdot}75\, P_j}{R_j} = 0{\cdot}5833\, Be\, E_0 e^{-\mu} r \sum_j \frac{P_j}{R_j} \tag{14}$$

The quantity $0{\cdot}5833r$ is the calculated average path of α-particles from the three nuclei; however, LIND and BARDWELL[11] experimentally determined a value of $0{\cdot}61\ r$, which is used in subsequent discussion and calculation in this report.

Reactors used in the present work, with the exception of the first few, were not spherical; instead they were composed (Fig. 1) of a cylindrical section that constituted the main volume, a section of small-bore tubing, and the Booth–Cromer pressure transmitter. LIND[1] has quoted LUNN to the effect that the average path in a cylinder of diameter nearly equal to its length is about the same as that in a sphere of the same volume. Thus, designating as V_r the main reaction volume, the effective radius of this unit is

$$r = \left[\frac{3V_r}{4\pi} \right]^{1/3}, \tag{15}$$

and the average path of an α-particle may be written as

$$L = 0{\cdot}61\ r = 0{\cdot}379[V_r]^{1/3}. \tag{16}$$

Dissociation of uranium hexafluoride also occurs in the small bore lines and in the pressure transmitter. However, the α-particle paths in these sections are considerably smaller than the paths in the volume V_r. A reasonable estimate is given by assuming α-particle utilization in these short-path sections to be only 15 per cent as efficient as it is in the volume V_r. The effective value of the randon charge, E'_t, is then given by equation (17).

$$E'_t = E_t \left[\frac{V_r}{V_s} + 0{\cdot}15 \frac{V_s - V_r}{V_s} \right] = \left[0{\cdot}15 + 0{\cdot}85 \frac{V_r}{V_s} \right] E_t \tag{17}$$

[11] S. C. LIND and D. C. BARDWELL, *J. Amer. Chem. Soc.* **45**, 2585 (1923).

By inserting the right-hand term of equation (17) and equation (16) into (14), we obtain the rate of energy absorption for the reactors actually used.

$$\frac{dE_a}{dt} = (0{\cdot}379\, V_r^{1/3})\, eB \left(0{\cdot}15 + 0{\cdot}85 \frac{V_r}{V_s}\right) E_0\, e^{-\lambda t} \sum \frac{P_j}{R_j} \tag{18}$$

As described previously, the effects of α-particles on uranium hexafluoride can be described in terms of reactions (1) and (4), the first of these summarizing decomposition, the second, reformation of the hexafluoride. It is apparent that k_1 of equation (2) actually contains the efficiency factor of equation (17), i.e.

$$k_1 = k'_1 \left(0{\cdot}15 + 0{\cdot}85 \frac{V_r}{V_s}\right). \tag{19}$$

The number rate of decomposition of uranium hexafluoride by reaction (1) is

$$\frac{dN}{dt} = AV_s \frac{dP_{UF6}}{dt} = AV_s k_1 P_{UF_6} E_0\, e^{-\lambda t}. \tag{20}$$

Then G_T, given by 100 times the ratio of quantities in equations (18) and (20), is as follows:

$$G_T = \frac{100 AV_s k_1 P_{UF_6}}{0{\cdot}379 V_r^{1/3}\, eB \left(0{\cdot}15 + 0{\cdot}85 \frac{V_r}{V_s}\right) \sum\limits_j \frac{P_j}{R_j}}, \tag{21}$$

or

$$G_T = \frac{100 AV_s k'_1 P_{UF_6}}{0{\cdot}379 V_r^{1/3}\, eB \sum\limits_j \frac{P_j}{R_j}}. \tag{22}$$

The summation in the denominator contains a term for uranium hexafluoride and one for fluorine. Since the pressure of fluorine was usually less than one-tenth that of the uranium hexafluoride, and since R_{F_2} is in the order of seven times R_{UF_6}, this summation may be replaced by P_{UF_6}/R_{UF_6}, whence equation (21) reduces to

$$G_U = \frac{100 AV_s k_1 R_{UF_6}}{0{\cdot}379 V_r^{1/3}\, eB \left(0{\cdot}15 + 0{\cdot}85 \frac{V_r}{V_s}\right)}. \tag{23}$$

As indicated previously, the absence of experimental range data has necessitated estimation of such quantities. For this purpose the correlation of STEIDLITZ *et al.*,[12] equation (24), has been used.

$$R = \delta V_0^3 / \sum_j n_j Z_j^{2/3} \tag{24}$$

$\delta = 6{\cdot}75 \times 10^{-26}$ mm $\left(\frac{\text{sec}}{\text{cm}}\right)^3$

V_0 = initial velocity of α-particle

n_j = number of atoms of atomic number Z_j

From equation (24) the average range of the three α-particles in uranium hexafluoride is 5·72 mm and in fluorine, 42·54 mm.

[12] M. E. STEIDLITZ, F. D. ROSEN, C. H. SHIFLETT and W. DAVIS, JR., *J. phys. Chem.* **56**, 803 (1952).

On the basis of equation (23), values of G_U have been calculated for those experiments in which the radon charge was measured. These are listed in Table 5. In addition to G_U there are listed values of M/n. The latter have been calculated by replacing the 100 eV term in equation (23) by 30 eV. This choice is somewhat arbitrary, but is consistent with the average energy required to produce one ion pair in a number of fluorocarbons.[12]

In any system in which radon is intimately mixed with the reacting gas, the recoil

TABLE 5.—VALUES OF G_U AND M/n

Expt. No.	V_s	V_r	G_U	M/n
	cm³	cm³	molecules/100 eV	molecules/ion pair
5	35·9	31·4	0.76	0·23
24	7·4	6·7	1·40	0·42
16	11·4	9·5	0·96	0·29
15	10·5	8·6	1·13	0·34
7	10·5	8·6	1·04	0·32
31	7·1	5·5	0·59	0·18
33	7·1	5·5	1·14	0·34
36	7·1	5·5	0·59	0·18
34	7·1	5·5	0·47	0·14
		95% C.I	0·90 ± 0·73	0·27 ± 0·22

atoms cause some ionization. However, this effect amounts only to a 3 per cent reduction in the M/n values with the conditions of geometry and pressure employed in these studies. Hence, these effects may well be neglected.

Re-formation of uranium hexafluoride

In order to facilitate an understanding of the back reaction, two of the reactors which had been used in studies of the decomposition of uranium hexafluoride were re-used with a mixture of fluorine and uranium hexafluoride, experiments 8 and 9. Under these conditions the pressure of uranium hexafluoride increased, and later decreased, as shown in Fig. 3. While the uranium hexafluoride pressure passed through a maximum, the fluorine pressure went through a minimum. It is noteworthy that the maximum uranium hexafluoride pressure occurred when the solid fluoride had been converted almost 100 per cent to uranium hexafluoride. Data of experiments 8 and 9 were divided as follows: group 1, taken before the maximum uranium hexafluoride pressure was attained; group 2, taken after this maximum. Values of the constants so calculated are listed in Table 6. It is apparent from this table that, within experimental error, k_1 is constant throughout the course of reaction. However, the group 1 value of $k_2(S)$ is larger in both experiments than the group 2 value. The data thus suggest that during the interim between the completion of a decomposition experiment and subsequent re-use of a vessel, the UF_z deposit becomes more reactive toward

TABLE 6.—RATE CONSTANTS OF EXPERIMENTS 8 AND 9

Run No.	Temp. (°C)	UF_6 decomposition $k_1 \times 10^5$ (c^{-1} sec^{-1})	UF_6 formation $k_2(S) \times 10^6$ (c^{-1} sec^{-1})	Initial F_2 press. (cm)
8—Group 1	63	3·16	16·52	10·4
8—Group 2	63	2·82	10·49	
9—Group 1	65	3·96	53·94	5·1
9—Group 2	65	4·06	21·66	

α-particle induced fluorination to UF_6. Two factors that may be involved in this activation are crystal growth and evacuation of the reactor.

Effect of temperature

Experiments were performed at temperatures ranging from 26 to 87°C. Although there is a considerable spread in the data, Tables 4 and 5, values of G_U or M/n do not show any increase with temperature. This lack of temperature dependence is expected, since temperature, within limits, does not have any appreciable effects on ionization processes and, in addition, would have little effect on the efficiency of any electronic excitation process over this small temperature range. It is apparent, however, that as the temperature is increased toward 200–300°C, thermal reaction of fluorine and uranium fluorides would become important.[9]

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THE PREPARATION OF ANHYDROUS INORGANIC CHLORIDES BY DEHYDRATION WITH THIONYL CHLORIDE

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Abstract—The anhydrous chlorides of a number of the lanthanides, thorium, magnesium and other elements have been prepared by refluxing the hydrated chlorides with thionyl chloride. The preparation is simple and effective and gives a product which is free from oxychloride or oxide. The method is of general application to elements whose oxides are not acidic or amphoteric and which are not oxidized by thionyl chloride.

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MOST of the source materials used in the electromagnetic isotope separators at A.E.R.E. are fused anhydrous chlorides. The programme of separation requires the preparation of these from a variety of polyisotopic elements, some radioactive, in quantities ranging from a few milligrams to several kilograms.

Because of the importance of anhydrous chlorides in metallurgical work and basic chemical research, there is a large field of literature devoted to their preparation, but most methods require high temperature or vacuum processing. Moreover, results on quantities of a few hundred grammes are often irreproducible and the products contain varying quantities of oxide and oxychloride. Some of the methods which have been used for source preparation are described in more detail below.

Action of ammonium chloride on the oxide

REED *et al.*[1] recommended heating the lanthanide oxide with an excess of ammonium chloride and then removing the volatile ammonium chloride under vacuum at 300°C. They obtained yields of 85–90 per cent with lanthanum, neodymium and praseodymium oxides but do not appear to have prepared the chlorides of the higher lanthanides. This is the standard procedure at ORNL[2] for the preparation of lanthanide chlorides. RICHARDS[3] used the hydrated chlorides and removed the ammonium chloride by heating in a steam of dry nitrogen for several hours. He obtained good results with neodymium chloride but the products from samarium and gadolinium chlorides contained varying amounts of oxide and oxychloride. The authors have had excellent yields of thorium tetrachloride by this method. SPRAGG[4] has obtained good results by freezing out a solution of ammonium chloride and lanthanum chloride and removing the water and ammonium chloride by vacuum distillation. The method is a useful one for gramme quantities but it is tedious and lengthy for large scale preparations.

[1] J. B. REED, B. S. HOPKINS and L. F. AUDRIETH, *J. Amer. Chem. Soc.* **57**, 1159 (1935).
[2] *U.S.A.E.C. Report* ORNL-2028 (1952).
[3] C. E. C. RICHARDS, A.E.R.E. Private communication.
[4] W. SPRAGG, A.E.R.E. Private communication.

Dehydration by hydrogen chloride

KLEINHEKSEL and KREMERS[5] found that hydrated chlorides could be dehydrated by heating for several days in an atmosphere of dry hydrogen chloride at low pressure. HARRISON[6] obtained poor yields by this method and obtained purer products by heating the hydrated chloride at 500°C or more in a stream of hydrogen chloride at atmospheric pressure. RICHARDS[3] used a high temperature and low pressure in his preparations.

This method has been extensively used at Harwell for source preparations, but it is lengthy and requires frequent attention. It does not give good yields with the higher lanthanides.

Chlorination of the benzoate

The anhydrous chlorides of the cerium metals can be prepared in good yields by the method of BRAUMAN.[7] The dried benzoate is treated with successive washings of anhydrous ether saturated with hydrogen chloride. The conversion to the chloride is quantitative and the product very pure. The authors have modified the method by passing dry hydrogen chloride into an ether suspension of the benzoate.

The difficulties of preparing and dehydrating the benzoate, and of handling large volumes of anhydrous ether limit the use of this method to small scale preparations.

Chlorination by carbon tetrachloride

The action of carbon tetrachloride in the vapour state on the heated oxide is well established as a method of preparing anhydrous chlorides.

It is difficult to obtain quantitative conversion by this method and thorium tetrachloride can only be prepared by subliming off the product from the thoria.

Chlorination by hexachloropropene

Uranium tetrachloride can readily be prepared by refluxing U_3O_8 with hexachloropropene for about 4 hr. Plutonium trichloride[8] can be similarly prepared by prolonged heating of plutonium sesquioxalate in hexachloropropene. The authors were unable to prepare the chlorides of thorium or the rare earths by this method.

PREPARATION WITH THIONYL CHLORIDE

The hydrated chlorides of thorium, the lanthanides and several other elements can be readily dehydrated by refluxing with thionyl chloride according to the reaction:

$$MCl_n\, xH_2O + xSOCl_2 \rightarrow MCl_n + xSO_2 + 2xHCl$$

Thionyl chloride has been employed in the gaseous phase and in the liquid phase at high pressures[9] as a chlorinating agent. It was first used as a dehydrating agent by HECHT[10] for the preparation of a number of mono- and bi-valent anhydrous chlorides.

[5] J. H. KLEINHEKSEL and H. C. KREMERS, *J. Amer. Chem. Soc.* **50**, 959 (1928).
[6] E. R. HARRISON, *AERE*/G/R-929).
[7] P. BRAUMAN and S. TAKVORIAN, *C.R. Acad. Sci. URSS* **194**, 1579 (1932).
[8] *U.S.A.E.C. Report LA*-1431 (1952).
[9] *Radiochemical Studies: The Chemistry of Uranium* (Edited by C. D. CORYELL and N. SUGARMAN) NNES, Plutonium Project Record, Div. 5, Vol. 8. McGraw-Hill, New York (1949).
[10] H. HECHT, *Z. Anorg. Chem.* **254**, 37 (1947).

The preparation with thionyl chloride has the following advantages:

(1) Apparatus is simple and generally available.
(2) The preparation is carried out at a low temperature.
(3) No precautions need to be taken against the presence of moisture or air during the preparation.
(4) The by-products are dry gases which can be eliminated in a normal fume hood. The reaction is stoicheiometric and the quantity of HCl produced is low.
(5) The starting materials (hydrated chlorides and thionyl chloride) can be readily obtained.
(6) The reaction is fairly rapid, except in the cases of certain of the lanthanide chlorides and a complete preparation even on a large scale can be carried out in a few hours with a minimum of operations.

Under the experimental conditions described, thionyl chloride does not act as a chlorinating agent and will not for example convert lanthanide oxychlorides to the anhydrous chlorides. Little information on free energies of hydration is available and it is not possible to predict which chlorides may be dehydrated in this way.

It is interesting to note that the chlorides of the lanthanides of higher atomic weight are more difficult to dehydrate and that the ease of dehydration corresponds roughly to the heat of hydration of the chloride.[11]

The variation in reaction time is in striking contrast to the normal chemical behaviour of the lanthanides. The dehydration times given below are for lanthanides of purity >97 per cent, but it was found that "spec pure" lanthanides required a considerably longer dehydration time and that mixtures of lanthanide chlorides required a much shorter reaction time than had been anticipated. The reason for the "activation" in mixtures is not known.

TABLE 1.—THE HEATS OF HYDRATION OF THE LANTHANIDE CHLORIDES AND THE REACTION TIME FOR DEHYDRATION WITH THIONYL CHLORIDE

Lanthanide	La	Ce	Pr	Nd	Sm	Gd	Dy	Er
Heat of hydration (kcal)	31·6	32·7	33·9	35·9	39	42·4	47·3	49·5
Approx. time for dehydration (hr)	1	3	4	4	5	15	50	110

EXPERIMENTAL

The hydrated chloride is ground to a fine powder, transferred to a flask fitted with a reflux condenser, an excess of thionyl chloride is added and the mixture refluxed until the dehydration is complete. The thionyl chloride should be colourless and care must be taken not to overheat the flask as this may cause some decomposition of the thionyl chloride, and may convert the hydrated chloride to oxychloride. Deliquescent chlorides (e.g. $CeCl_3$) which cannot readily be ground may be dried by treating with a small quantity of thioynl chloride before grinding. Oven drying is not recommended as the products are unreactive in some cases. For preparations where the solid chloride is not available, a concentrated solution of the chloride in HCl can be treated directly with an excess of thionyl chloride and refluxed as above. This method gives a very fine crystalline product which does not require grinding prior to dehydration, and gives a rapid preparation from the hydroxide, oxide, or carbonate which can be dissolved in hydrochloric acid.

[11] H. BOMMER and E. HOHMANN, *Z. Anorg Chem.* **248**, 376 (1941).

The course of the reaction can be followed (except for $FeCl_3$) by removing a very small quantity of solid from time to time and heating this to red heat on a small platinum boat in a stream of nitrogen or argon. When the heated solid is completely soluble in water the dehydration is complete.

On completion of the reaction, the remaining thionyl chloride can be distilled off or decanted, and the solid dried by warming, preferably in a steam of dry nitrogen or argon. Products from lengthy preparations may contain some sulphur. This can be removed by heating strongly in a stream of nitrogen.

Some typical preparations are summarized below. The reaction products were identified by chemical analysis, X-ray diffraction studies and volatility *in vacuo*.

Because of the low molecular weight of water, accurate analyses (>99·9 per cent) of the chlorides are required to confirm their complete dehydration. The very hygroscopic nature of most polyvalent anhydrous chlorides makes such a degree of accuracy difficult to achieve and a more satisfactory measure of the completeness of dehydration is given by the degree of volatility *in vacuo*. All of the products described below were heated for 2 hr at 950°C *in vacuo* and were found to be completely volatile. Chemical analyses (>95 per cent accuracy) were carried out only to confirm the formulae of the chlorides and to show the absence of addition compounds with thionyl chloride. X-ray powder photographs of Th, La, Ce, Pr, Nd, and Gd were taken. The lines on these diffraction patterns could be indexed in terms of the unit cell dimensions proposed by MOONEY[12] and ZACHARIASEN.[13]

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Lanthanides

	(All samples better than 97 per cent pure)
$LaCl_3$	50 g $La(NO_3)_3$ ignited, dissolved in the minimum of 50 per cent HCl, refluxed with excess $SOCl_2$; reaction time 1hr.
$CeCl_3$	20 g $CeCl_3$, nH_2O dried with $SOCl_2$, ground and refluxed; reaction time 3 hr.
$NdCl_3$	5 g $NdCl_3 6H_2O$ ground and refluxed; reaction time 4 hr.
$PrCl_3$	As for $NdCl_3$; reaction time 5 hr.
$SmCl_3$	As for $NdCl_3$; reaction time 5 hr.
$GdCl_3$	Several batches 5–600 g; reaction time 10–15 hr. The reaction proceeded more readily with the chloride prepared by adding $SOCl_2$ to the HCl solution than with chloride crystallized, and ground down.
$DyCl_3$	2 g Dy_2O_3 dissolved HCl refluxed with excess $SOCl_2$; reaction time approx. 50 hr
$ErCl_3$	0·5 g Er_2O_3 as for Dy; reaction time 110 hr.

Common metals

$FeCl_3$	$FeCl_3$, nH_2O dissolves in excess $SOCl_2$. The $SOCl_2$ can be distilled off leaving pure $FeCl_3$.
$FeCl_2$	Reacts with $SOCl_2$ to give $FeCl_2$ and sulphur.
$MgCl_2$	500 g ground $MgCl_2 6H_2O$ refluxed; reaction time approx. 24 hr.
$CuCl_2\ 2H_2O$	Reacts in cold to give $CuCl_2$.

Actinides

$ThCl_4$	100 g $ThCl_4 nH_2O$ ground and refluxed; reaction time 4 hr.
$PuCl_3$	Attempts to prepare $PuCl_3$ from solutions of Pu^{3+} or Pu^{4+} in hydrochloric acid resulted in an unidentified brown solid which contained sulphate ions and free sulphur. It appears that the following reaction takes place in solution.

$$Pu^{3+} + SOCl_2 \rightarrow Pu^{4+} + S$$

$$Pu^{4+} + SO_2 \rightarrow Pu^{3+} + SO_2$$

Although the preparation of $PuCl_3$ was not successful it seems probable that the method could be used for those actinides which are more stable in the trivalent stage e.g. actinium, americium, curium and californium.

Acknowledgements—The authors are grateful to R. W. M. D'EYE and I. FERGUSON for X-ray diffraction data, and to J. REYNOLDS for assistance with some of the preparations.

[12] R. C. L. MOONEY, *Acta Cryst.* **2**, 189 (1949).
[13] W. H. ZACHARIASEN, *Acta Cryst.* **1**, 265 (1948).

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THE REACTION OF ALUMINIUM CHLORIDE WITH LITHIUM BOROHYDRIDE*

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Abstract—The synthesis of aluminium borohydride by the reaction between lithium borohydride and aluminium chloride seems to occur, at least in part, through the decomposition of very unstable, volatile intermediates. Attempts to isolate these intermediates in pure state were unsuccessful but by trapping intermediate fractions at low temperatures and destroying them with excess hydrogen chloride, it was possible to obtain analytical evidence consistent with the identification of the intermediate compounds as $Al(BH_4)Cl_2$ and $Al(BH_4)_2Cl$.

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ALUMINIUM borohydride is one of the products of the reaction between lithium borohydride and aluminium chloride, as reported by SCHLESINGER *et al.*[1] The complexity of this reaction is shown by the simultaneous formation of hydrogen, diborane, and other products unidentified. Additional evidence of its complexity was obtained by GOODSPEED,[2] who attempted to obtain $Al(BH_4)_3$ by a modification of the above method. The main difference was in the fractionation of the volatile products, although he also used larger excesses of $AlCl_3$. The original authors allowed the entire volatile, condensable fraction to warm to 25° and then to diffuse through traps at selected temperatures, thus obtaining good yields of $Al(BH_4)_3$. GOODSPEED attempted to fractionate either by gradually increasing the condensate temperature from −196°, or by allowing the initial volatile products to diffuse continuously during the reaction, through successively colder traps. In the fractions as volatile as $Al(BH_4)_3$ or more, little or no borohydride was found. However, when less volatile fractions were warmed to 25°, $Al(BH_4)_3$ was rapidly evolved, along with diborane and hydrogen. Evidently GOODSPEED's modification resulted in the isolation of relatively large amounts of unstable intermediates either unobserved, or observed only in traces, in the original synthesis.

We have investigated further, obtaining evidence that the major intermediates in the formation of $Al(BH_4)_3$ by reaction of $LiBH_4$ with $AlCl_3$ are mixtures or combinations of the chloroborohydrides, of empirical formula $Al(BH_4)Cl_2$ and $Al(BH_4)_2Cl$, originally reported by HOEKSTRA and KATZ[3] as resulting from the action of $Al(BH_4)_3$ on $TiCl_4$. The former appears to be an unstable volatile solid and the latter a very unstable liquid melting at about −10° (very tentative; purity not established). Similar products are indicated to result, we have found, from the very slow interaction of $Al(BH_4)_3$ vapour with $AlCl_3$ at 25°, or rapidly by the reaction of HCl with excess $Al(BH_4)_3$ at −78·5°.

* Taken from a dissertation presented by W. M. OLSON in partial fulfillment of the requirements for the Ph.D. degree, State University of Iowa, 1958.

[1] H. I. SCHLESINGER, H. C. BROWN and E. K. HYDE, *J. Amer. Chem. Soc.* **75**, 209 (1953).
[2] N. C. GOODSPEED, PhD. Thesis, State University of Iowa (1956); *Diss. Abstr.* **16**, 648 (1956).
[3] H. R. HOEKSTRA and J. J. KATZ, *J. Amer. Chem. Soc.* **71**, 2488 (1949).

EXPERIMENTAL

Aluminum chloride was sublimed *in vacuo* into the reactor and the residue was sealed off. The reactor was then closed and removed to a dry box. There $LiBH_4$ (obtained by metathetical reaction of 98% $NaBH_4$ with LiCl in *iso*propyl amine, removal of the amine and extraction with ether) was added to a separate part of the reactor. This was then reattached to the vacuum line and re-evacuated. The reactants were mixed by rotating the tube about a ground joint. Reaction began at once.

The instability of both chloroborohydrides prevented their isolation in pure state, for at temperatures where they are volatile, they continuously form H_2, B_2H_6, and $Al(BH_4)_3$, and unidentified much less volatile products. We therefore attempted, using standard high vacuum techniques,[4] to separate fractions of the products less volatile than $Al(BH_4)_3$, condensing them as soon as they diffused from the reactor, in specially designed traps (usually held at −23° and −45°) which were then sealed from the vacuum line and held at −196°. To each trap, opened to the vacuum system through a tube opener, was added a measured excess of HCl. The trap was then resealed from the line, and warmed slowly to room temperature, allowing the HCl to destroy the BH_4 groups, primarily by the reaction.[5]

$$Al\text{-}BH_4 \quad HCl \rightarrow Al\text{–}Cl + \tfrac{1}{2}B_2H_6 + H^2$$

The tube was then reopened to the vacuum system, the H_2 pumped into a gasometer and measured, the B_2H_6–HCl fraction measured and then analysed, and the remainder analysed by standard procedures for B, Al, and Cl.

RESULTS AND DISCUSSION

Results from a number of experiments are summarized in Tables 1 and 2. Among the volatile products of the overall reaction, we found no more than unidentified traces of substances other than H_2, B_2H_6, $Al(BH_4)_3$, $Al(BH_4)_2Cl$, and $Al(BH_4)Cl_2$. The occasional but not consistent appearance of $AlCl_3$ in the first trap probably was due to the impossibility of duplicating the reaction conditions when the reaction is between solids for which the degree of mixing is of necessity somewhat fortuitous. The amount of entrainment of $AlCl_3$ would depend on the rate of evolution of volatile products and their rate of diffusion through the reactor and traps. There is also a possibility that some of the $AlCl_3$ in the first trap could have been formed by a

TABLE 1.—$AlCl_3$–$LiBH_4$ REACTIONS AND VOLATILE PRODUCTS

Exp. no.	Temp. (°C)	Time (hr)	Reactants $LiBH_4$	(mmole) $AlCl_3$	Products (mmole)				
					H_2	B_2H_6	$Al(BH_4)_3$	$Al(BH_4)_2Cl$*	$Al(BH_4)Cl_2$*
1	100	3–4	9·94	excess	1·03	present	present	0·95	—
2	25–70	3	5·49	excess	0·95	present	present	0·05	0·13
3	70	3–4	6·71	23·32	0·19	0·11	0·80	0·03	0·34
4	25–70	4	8·76	27·53	0·10	0·14	2·09	0·01	1·13
5	25–70	4	10·96	24·69	0·13	0·60	2·50	0	0·51

* Identified in mixtures: see Table 2.

[4] R. T. SANDERSON, *Vacuum Manipulation of Volatile Compounds*. Wiley, New York (1948).
[5] H. I. SCHLESINGER, R. T. SANDERSON and A. B. BURG, *J. Amer. Chem. Soc.* **62**, 3421 (1940).

Table 2.—Identification of volatile intermediate products

Exp. no.	Products (mmole)	Al	B	H	Cl
1	$0{\cdot}95Al(BH_4)_2Cl$	0·95	1·90	7·60	0·95
	found (non-vol. −55°)	1·00	1·90	7·61	0·90
2	$0{\cdot}026AlCl_3$ + $0{\cdot}131Al(BH_4)Cl_2$	0·16	0·13	0·52	0·34
	found (non-vol. −23°)	0·16	0·12	0·52	0·37
	$0{\cdot}02Al(BH_4)_3$ + $0{\cdot}05Al(BH_4)_2Cl$	0·07	0·16	0·64	0·05
	found (non-vol. −45°)	0·09	0·16	0·64	0·05
3	$0{\cdot}294Al(BH_4)Cl_2$	0·29	0·29	1·18	0·59
	found (non-vol. −23°)	0·31	0·43	1·18	0·62
	$0{\cdot}049Al(BH_4)Cl_2$ + $0{\cdot}033Al(BH_4)_2Cl$	0·08	0·12	0·46	0·13
	found (non-vol. −45°)	0·07	0·11	0·46	0·13
4	$1{\cdot}071Al(BH_4)Cl_2$ + $0{\cdot}436AlCl_3$	1·51	1·07	4·28	3·44
	found (non-vol. −23°)	1·51	1·02	4·28	3·50
	$0{\cdot}056Al(BH_4)Cl_2$ + $0{\cdot}014Al(BH_4)_2Cl$	0·07	0·09	0·33	0·12
	found (non-vol. −45°)	0·08	0·11	0·33	0·12
5	$0{\cdot}248Al(BH_4)Cl_2$ + $0{\cdot}446AlCl_3$	0·69	0·25	0·99	1·83
	found (non-vol. −23°)	0·69	0·25	0·99	1·90
	$0{\cdot}266Al(BH_4)Cl_2$	0·27	0·27	1·07	0·53
	found (non-vol. −45°)	0·27	0·26	1·07	0·55

disproportionation reaction of chloroborohydrides in transit, and again this would depend on the unregulatable conditions of reaction.

In order to account for the formation of the hydrogen and diborane, it would be necessary to examine in detail the nonvolatile residues from such reactions. Our own studies, although thus far inconclusive, have suggested that among the residual materials may be non-volatile hydrides of boron, hydrides or chlorohydrides of aluminium, and borohydride complexes with aluminium chloride. Further studies may be extremely difficult, but will be essential for a more complete understanding of what occurs.

J. Inorg. Nucl. Chem., 1958, Vol. 7, pp. 231 to 244. Pergamon Press Ltd., London

HYDROGEN BONDING IN ORGANOPHOSPHORIC ACIDS*

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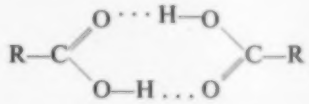
Abstract—Association in organophosphoric acids due to hydrogen bonding appears to be stronger than that in monocarboxylic acids. Molecular weights obtained by freezing-point studies show that the following monobasic phosphoric acids are dimeric in benzene and naphthalene: bis-(2-ethylhexyl), bis-(phenyl), bis-(2,6-dimethylheptyl-4), bis-[*p*-(1,1,3,3-tetramethylbutyl)phenyl] and bis-(*n*-butyl). The dibasic phosphoric acids, mono-(2-ethylhexyl) and mono-[*p*-(1,1,3,3-tetramethylbutyl) phenyl] were found to be polymeric in these solvents. Distribution studies of these acids between immiscible organic phases gave additional information as to their states of aggregation, and in addition indicated the strong interaction between these acids and a hydrogen bonding solvent, such as ethylene glycol. Infra-red studies of these acids in carbon tetrachloride show that no non-associated OH spectra appear in the fundamental and overtone regions.

THE association of monocarboxylic acids has been reported.[1–21] It is generally accepted that the asociation is due to intermolecular hydrogen bonding and that the structure of the dimer[1–3] is



In inert solvents such as naphthalene and benzene the monocarboxylic acids show abnormally high molecular weights. In carbon tetrachloride at high dilutions some monomerization occurs.[4–10] This association of monocarboxylic acids was studied by infra-red spectrophotometry.[4–11]

* Based on work performed under the auspices of the U.S. Atomic Energy Commission. Paper presented at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy held in Pittsburgh, Pa. March 3–7 (1958).

[1] N. U. SIDGWICK, *Ann. Rep.* **30**, 114–115 (1930).
[2] L. PAULING, *Nature of the Chemical Bond*. Cornell University Press (1948).
[3] J. KARLE and L. O. BROCKWAY, *J. Amer. Chem. Soc.* **66**, 574 (1944).
[4] W. GORDY, *J. Chem. Phys.* **5**, 284 (1937).
[5] M. M. DAVIES and G. B. SUTHERLAND, *J. Chem. Phys.* **6**, 755 (1938).
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[12] B. C. BARTON and C. A. KRAUS, *J. Amer. Chem. Soc.* **73**, 4561 (1951).
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[14] M. DAVIES, P. JONES, D. PATNAIK and E. A. MOELWYN-HUGHES, *J. Chem. Soc.* 1249 (1951).
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[16] C. P. BROWN and A. R. MATHIESON, *J. Phys. Chem.* **58**, 1057 (1954).
[17] G. M. BARROW and E. A. YERGER, *J. Amer. Chem. Soc.* **76**, 5248 (1954).
[18] M. M. DAVIES and D. M. L. GRIFFITHS, *Z. Physik. Chem.* (N.F.), **2**, 353 (1954).
[19] D. R. CARTWRIGHT and C. B. MONK, *J. Chem. Soc.* 2500 (1955).
[20] M. M. DAVIES and D. M. L. GRIFFITHS, *J. Chem. Soc.* 132 (1955).
[21] B. HÖK-BERNSTRÖM, *Acta Chem. Scand.* **10**, 174 (1956).

Recently we have prepared several organophosphoric acids in our laboratory in purity of better than 99 per cent. These acids have been found to be excellent solvents for various cations.[22–24] Preliminary molecular weights obtained by the freezing point lowering of benzene showed the organophosphoric acids to be polymeric.[25] It was suggested that the dimeric monobasic phosphoric acids $[(GO)_2PO(OH)]_2$ may be represented also as an eight-membered ring involving hydrogen bonding, similar to the monocarboxylic acids. The complexity of the polymeric dibasic phosphoric acids $[(GO)PO(OH)_2]_x$ was also explained in terms of hydrogen bonding. In an effort to study this association further, additional freezing point studies, distribution studies between immiscible phases, and an infra-red investigation were made on these acids; and this paper describes the results obtained.

EXPERIMENTAL

Preparation and purification of organophosphorus solvents

The general scheme of separation reported by PEPPARD *et al.*[22] based on the technique developed by STEWART and CRANDALL,[26] was modified in several important respects so that any $(GO)_3PO$ and GOH initially present and any GOH formed during the pyrophosphoric ester destruction step might be removed and so that the mutual separation of $(GO)_2PO(OH)$ and $(GO)PO(OH)_2$ might be accomplished more readily.

The same general procedure was followed for the three pairs of mono- and di-esters where G is respectively 2-ethylhexyl (Victor Chemical Works), *p*-(1,1,3,3 tetramethylbutyl)phenyl (Victor Chemical Works), and 2,6-dimethylheptyl-4 (Hooker Chemical Co.). In the last case, only the di-ester was isolated in high purity. The specific procedure employed in the separation of the 2-ethylhexyl compounds is as follows.

A 1 l. portion of the mixture, about a 60:40 molar ratio of di-ester to mono-ester, is stirred with 300 ml of 6 M HCL at 80°C for 8 hr to convert any pyro esters to ortho esters. (Some hydrolysis to form GOH is to be expected in this step.)

The aqueous HCl phase is discarded and the cooled organic phase washed with a 300 ml portion of water to remove the major fraction of the HCl content. This washed mixture is then neutralized by the addition of 1 M NaOH, and a slight excess of 1 M NaOH is added. (At this point two liquid phases are present provided the initial feed had a composition varying between 1:10 and 10:1 molar ratio of mono- and di-esters. The upper phase contains the major portion of the di-ester and the lower phase contains the major portion of the mono-ester. If only the di-ester is desired, a rapid purification may be accomplished by scrubbing this upper phase with several portions of 0·5 M NaOH).

To the mixture of these two liquid phases is added approximately 4 l. of diethyl ether. Following stirring there are two liquid phases, the upper (ether) phase containing the major portion of the di-ester as the sodium salt and the lower (aqueous) phase containing the major portion of the mono-ester as the sodium salt.

[22] D. F. PEPPARD, G. W. MASON, J. L. MAIER and W. J. DRISCOLL, *J. Inorg. Nucl. Chem.* **4**, 334 (1957).
[23] D. F. PEPPARD, S. W. MOLINE and G. W. MASON, *J. Inorg. Nucl. Chem.* **4**, 344 (1957).
[24] D. F. PEPPARD, G. W. MASON and S. W. MOLINE, *J. Inorg. Nucl. Chem.* **5**, 141 (1957).
[25] D. F. PEPPARD, J. R. FERRARO and G. W. MASON, *J. Inorg. Nucl. Chem.* **4**, 371 (1957).
[26] D. C. STEWART and H. W. CRANDALL, *J. Amer. Chem. Soc.* **73**, 1377 (1951).

The separated aqueous phase is then contacted with several portions of ether to remove traces of GOH and $(GO)_3PO$ and to further purify the mono-ester from contaminant di-ester. (Following acidification with HCl, the mono-ester is further purified by ethylene glycol–benzene partition as described below.)

The separated ether phase is contacted with several portions of 0·5 M NaOH to effect a further separation from the mono-ester. The ether is then removed by evaporation and the residue (still containing a small quantity of ether) dissolved by adding to a mixture of 2·5 l. of water and 1 l. of benzene. The equilibrated aqueous phase is then contacted with three 1 l. portions of benzene to remove alcohol and tri-ester. The aqueous phase is then acidified with a slight excess of 12 M HCl and the di-ester extracted into 2 l. of benzene. Following two water scrubs to remove HCl, the benzene phase is contacted with several 1 l. scrubs of ethylene glycol to further reduce the small content of contaminant mono-ester. Traces of ethylene glycol are then removed from the benzene phase by use of water scrubs. Finally, the benzene is removed at reduced pressure at approximately 40°C. Long pumping at 40°C and approximately 50 mm pressure serves to remove all of the water. (The sample is contained in a rotating 2 l. flask which creates a new surface continually. The pure material is very viscous.)

In like manner, the mono-ester is purified from contaminant di-ester by dissolving it in ethylene glycol and contacting the solution with several portions of benzene. The ethylene glycol phase is then diluted with an equal volume of water and the resultant solution contacted with diethyl ether. The ether phase, containing the mono-ester, is scrubbed with 0·2 M aqueous HCl to remove traces of ethylene glycol. Following removal of the major fraction of the ether by evaporation, the residual ether and water (and HCl) are removed from the mono-ester by long pumping at 40°C at 50 mm pressure, as in the final isolation of the di-ester.

In the separation of the *p*-(1,1,3,3-tetramethylbutyl) phenyl compounds the GO accompanies the mono-ester and is removed by fractional crystallization of the sodium salts from water.

The isolation of bis-(*n*-butyl) phosphoric acid, from the mixture obtained from Commercial Solvents, is considerably simpler than the above separations, involving the hydrochloric acid hydrolysis step, followed by conversion to an aqueous solution of sodium salts from which the alcohol and tri-ester are removed by benzene extraction. Following acidification, of the aqueous phase, the di-ester is extracted into ether and the residual mono-ester removed from the ether extract by water scrubbing. The major fraction of the ether is removed by evaporation. Residual ether and water are removed by pumping at approximately 50 mm pressure at 40°C.

Bis-(phenyl) phosphoric acid was prepared in excess of 90 per cent yield as follows. Tris-(phenyl) phosphate (Distillation Products, Eastman) was refluxed with a 50 per cent excess of 3 M aqueous NaOH for one hour. Following recrystallization of the resultant sodium salt, the salt was converted to the free acid by addition of hydrochloric acid. The acid was then recrystallized from water twice and finally pumped at about 10 mm pressure and 70°C to convert to the anhydrous form.

Physical properties of organophosphorus solvents

The equivalent weights of the solvents were obtained by standard alkali titration. Viscosity measurements were made in a water bath, controlled at a temperature of

20° ± 0·025°C. The water analyses were determined by standard Karl Fischer titration.[27] Table 1 lists the physical properties of the solvents used in this study.

Cryoscopic studies

The freezing-point studies were conducted in a standard Beckman type freezing-point apparatus using a Beckman differential thermometer. With the dibasic phos-

TABLE 1.—PHYSICAL PROPERTIES OF SEVERAL ORGANOPHOSPHORUS SOLVENTS

Solvent	Experimental equivalent weight	Density 20°/20°C	Index of refraction 25°C	Viscosity* (poises) 20°C	H_2O (%)
Bis-(2-ethylhexyl) phosphoric acid	322	0·975	1·4469	0·422	0·12
Bis-(phenyl) phosphoric acid	250	1·349†	—	—	nil‡
Bis-(*n*-butyl) phosphoric acid	209	1·060	1·4263	0·710	0·23
Bis-(2,6-dimethylheptyl-4) phosphoric acid	357	0·951	1·4359	1·347	0·19
Bis-[*p*-](1,1,3,3-tetramethylbutyl) phenyl phosphoric acid	483	1·048†	—	—	nil
Mono-(2-ethylhexyl) phosphoric acid	103	1·096	1·4421	16·013	0·27
Mono-[*p* (1,1,3,3-tetramethylbutyl) phenyl] phosphoric acid	142	1·135§	—	—	nil

* $\eta_1 = \frac{t_1 d_1}{t_2 d_2} \eta_2$ where $\eta_2 = 0{\cdot}010087$ poises at 20°C for water.

† By displacement of mercury.
‡ Less than 0·1% water considered nil.
§ By displacement of mineral oil.

phoric acids, small amounts of moisture were found to greatly affect the freezing-point determination and for these, a modified freezing-point apparatus was used which allowed the measurement to be done in a dry nitrogen atmosphere. The benzene was the "Spectral Grade" from Eastman Kodak Co. The naphthalene (recrystallized from alcohol) and the dioxane were also from Eastman Kodak Co. The acetic acid was obtained from the Mallinckrodt Chemical Works (analytical reagent). The ethylene glycol was obtained from Matheson Co. Inc. The diethyl ether (absolute) was from the J. T. Baker Chemical Co. The freezing-point constant was determined for benzene, with naphthalene (5·2); for naphthalene, with triphenylmethane (7·0), and for acetic acid, with benzene (3·98).

The results of the molecular weight determinations for the various monobasic and dibasic phosphoric acids we have prepared are shown below. (Throughout this paper the term molal is defined as the number of formula weights per 1000 g solvent.)

Bis-(2-ethylhexyl) phosphoric acid

Benzene	0·18 molal conc., $\Delta T = 0{\cdot}465°$, M.W. 628
Dioxane	0·30 molal conc., $\Delta T = 0{\cdot}649°$, M.W. 732
Naphthalene	0·17 molal conc., $\Delta T = 0{\cdot}583°$, M.W. 642
	0·14 molal conc., $\Delta T = 0{\cdot}533°$, M.W. 598
Acetic Acid	0·27 molal conc., $\Delta T = 0{\cdot}980°$, M.W. 343
Dimeric M.W. = 645	

[27] J. MITCHELL, JR. and C. M. SMITH, *Aquametry*. Interscience Publishers, New York (1948).

Bis-[p-(1,1,3,3-*tetramethylbutyl*)*phenyl*] *phosphoric acid*

Benzene	0·15 molal conc., $\Delta T = 0{\cdot}370°$, M.W. 975
Naphthalene	0·14 molal conc., $\Delta T = 0{\cdot}477°$, M.W. 963
Dimeric M.W. = 949	

Bis-(*phenyl*) *phosphoric acid*

Benzene	0·31 molal conc., $\Delta T = 0{\cdot}625°$, M.W. 626
	0·39 molal conc., $\Delta T = 0{\cdot}777°$, M.W. 643
Naphthalene	0·28 molal conc., $\Delta T = 0{\cdot}788°$, M.W. 621
Dimeric M.W. = 500	

Bis-(n-*butyl*) *phosphoric acid*

Benzene	0·38 molal conc., $\Delta T = 1{\cdot}111°$, M.W. 434
Naphthalene	0·16 molal conc., $\Delta T = 0{\cdot}580°$, M.W. 410
Dimeric M.W. = 418	

Bis-(2,6-*dimethylheptyl*-4) *phosphoric acid*

Benzene	0·32 molal conc., $\Delta T = 0{\cdot}891°$, M.W. 646
	0·36 molal conc., $\Delta T = 0{\cdot}949°$, M.W. 673
	0·41 molal conc., $\Delta T = 1{\cdot}082°$, M.W. 681
Naphthalene	0·11 molal conc., $\Delta T = 0{\cdot}434°$, M.W. 623
Dimeric M.W. = 701	

Mono(2-*ethylhexyl*) *phosphoric acid*

Benzene	0·24 molal conc., $\Delta T = 0{\cdot}163°$, M.W. 1565
	0·32 molal conc., $\Delta T = 0{\cdot}240°$, M.W. 1415
	0·39 molal conc., $\Delta T = 0{\cdot}317°$, M.W. 1333
Naphthalene	0·08 molal conc., $\Delta T = 0{\cdot}092°$, M.W. 1285
	0·17 molal conc., $\Delta T = 0{\cdot}178°$, M.W. 1399
	0·22 molal conc., $\Delta T = 0{\cdot}200°$, M.W. 1547
Acetic Acid	0·20 molal conc., $\Delta T = 0{\cdot}785°$, M.W. 210
Monomeric M.W. = 210	

Mono-[p-(1,1,3,3-*tetramethylbutyl*)*phenyl*] *phosphoric acid*

Naphthalene	0·12 molal conc., $\Delta T = 0{\cdot}100°$, M.W. 2335
	0·17 molal conc., $\Delta T = 0{\cdot}116°$, M.W. 2869
Acetic Acid	0·13 molal conc., $\Delta T = 0{\cdot}490°$, M.W. 300
Monomeric M.W. = 286	

Molecular weights for several other organophosphorus solvents were also determined for comparative purposes, and the results are shown below in Table 2 along with their source. These solvents were used as obtained commercially and were not further purified.

Distribution studies

In the distribution studies, approximately 20 ml of the phosphoric ester was diluted to 100 ml with thiophene-free benzene and the resultant solution contacted for 3 min with a 100 ml portion of ethylene glycol (water content approximately 0·7 per cent).

Complete separation of phases was assured by centrifugation. Following withdrawal of aliquots of each phase for titration with standard aqueous NaOH, 0·01 M and 0·1 M using phenolphthalein as indicator, the phases were recombined and further portions of each barren phase, benzene and ethylene glycol, added in such a way as to obtain the desired points.

TABLE 2.—MOLECULAR WEIGHTS OF ORGANOPHOSPHORUS SOLVENTS

Solvent	Experimental M.W. benzene	Theoretical M.W.
Tris-(*n*-butyl) phosphate (Eastman Kodak Co.)	263	266
Tris-(2-ethylhexyl) phosphate (Carbide & Carbon Co.)	408	434
Tris-(*n*-butyl) phosphite (Virginia-Carolina Chemical Corp.)	240	250
Tris-(2-ethylhexyl) phosphite (Virginia-Carolina Chemical Corp.)	399	419
Tris-(phenyl) phosphite (Eastman Kodak Co.)	295	310
Bis-(*n*-butyl)(*n*-butyl) phosphonate (Virginia-Carolina Chem. Corp.)	254	250
Tris-(*n*-butyl) phosphorothioate (Victor Chemical Co.)	274	282
Tris-(*iso*-octyl) phosphorothioate (Victor Chemical Co.)	414	454
Tris-(ethyl) phosphorothioate (Victor Chemical Co.)	193	198
Phenyl phosphonic acid (Victor Chemical Co.)	242*	157

* M.W. in Dioxane

Absorption measurements

The infra-red spectra were obtained by means of a Perkin-Elmer infra-red spectrophotometer, Model 21, using a sodium chloride prism. Spectra were made on liquid film, KBr disk, or on solvent-dissolved material. The near infra-red spectra were obtained in a Beckman Model DK spectrophotometer. The carbon tetrachloride used as a solvent in the spectral determinations was the "Spectral Grade" from Eastman Kodak Co.

DISCUSSION AND RESULTS

Cryoscopic studies

The cryoscopically determined molecular weights demonstrated that the monobasic and dibasic phosphoric acids were polymeric. The monobasic phosphoric acids [$(GO)_2PO(OH)$], having one acidic function, were found to be dimeric in benzene and naphthalene. The proposed structure of the dimer is illustrated in Fig. 1, where an eight-membered ring is formed as a result of hydrogen bonding. The dibasic phosphoric acids [$(GO)PO(OH)_2$], having two acidic functions, were found to be polymeric. Mono-(2-ethylhexyl) phenyl phosphonate [$(G'O)(G)PO(OH)$] has one acidic function, and was also found to be dimeric. The states of aggregation of these acids are similar to those obtained by KOSOLAPOFF[28] for phosphonic acids [$GPO(OH)_2$] and for phosphinic acids [$(G)_2PO(OH)$]. KOSOLAPOFF found the phosphonic acids to be hexamers and the phosphinic acids to be dimers. The dibasic phosphoric acids, like

[28] G. M. KOSOLAPOFF and J. S. POWELL, *J. Chem. Soc.* 3535 (1950).

the phosphonic acids, contain the $PO(OH)_2$ grouping and as a result of hydrogen bonding polymerize to aggregates of six monomeric units and possibly higher. The exact extent of polymerization is difficult to determine because of the high sensitivity of the dibasic phosphoric acids toward further polymerization in the presence of water. The monobasic phosphoric acids, in analogy to the phosphinic acids, contain the

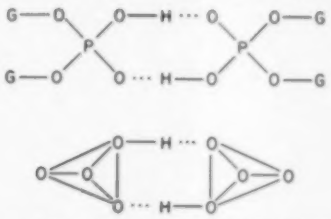


FIG. 1.—Proposed structure of $(GO)_2PO(OH)$ dimer.

POOH grouping* (similar to the COOH group in monocarboxylic acids) and, through formation of intermolecular hydrogen bonds, form dimers. The phosphonates [(G′O)(G)PO(OH)] also contain the POOH grouping and as expected were found to be dimers. It is of interest that the states of aggregations of these phosphoric acids are the same in benzene and in naphthalene, indicating that these polymers are very strongly hydrogen bonded even at higher temperatures.

With the monobasic phosphoric acids the molecular weights were found to increase as the concentration increases. This is the type of behaviour expected of polymers with molecular weights of less than 1000.[29,30] With the dibasic phosphoric acids the molecular weights were found to be readily increased by water, and to be greater than 1000. The effect of the increased concentration of these acids lowered the molecular weights. A similar behaviour has been found with polystyrene[23,30] polymers of molecular weights greater than 1000.

In acetic acid both the monobasic and dibasic phosphoric acids were found to give monomeric molecular weights. These results are interpreted as being due to solute–solvent interaction. It is believed that new hydrogen bonds are formed with the acetic acid thus causing the depolymerization observed. Similar results have been reported[31] with a number of organic acids and related compounds, which also showed monomeric molecular weights in hydrogen bonding solvents. These have been extensively discussed by LASSETTRE.[31] In many cases, water acts as a depolymerization solvent, and in it monomeric molecular weights are obtained. However, with the dibasic phosphoric acids the reverse has been observed and polymeric units are held together by molecules of water, thereby resulting in higher molecular weights.

Distribution studies

The liquid–liquid partition studies of bis-(2-ethylhexyl)† and bis-[*p*-(1,1,3,3-tetramethylbutyl)phenyl] phosphoric acids in benzene and ethylene glycol, and bis-(2-ethylhexyl) phosphoric acid in diethyl ether and ethylene glycol, indicated that these

* It is suggested that this group be called the "phosphoroxyl" group in analogy to the "carboxyl" group (COOH) in monocarboxylic acids.

† Henceforth will be abbreviated as HDEHP.

[29] C. E. H. BAUM, *Chemistry of High Polymers* p. 160. Interscience, New York (1948).
[30] A. R. KEMP and H. PETERS, *Industr. Engng. Chem.* **33**, 1263 (1941); **34**, 1097, 1192 (1942).
[31] E. N. LASSETTRE, *Chem. Rev.* **20**, 259 (1937).

acids are probably dimerized in the benzene phase and in the diethyl ether phase, and probably monomeric in the ethylene glycol phase. Fig. 2 shows the log-log plots of the acid concentration in the benzene phase and that in the ethylene glycol phase. Straight lines with slopes close to 2 were obtained. Apparently ethylene glycol breaks up the

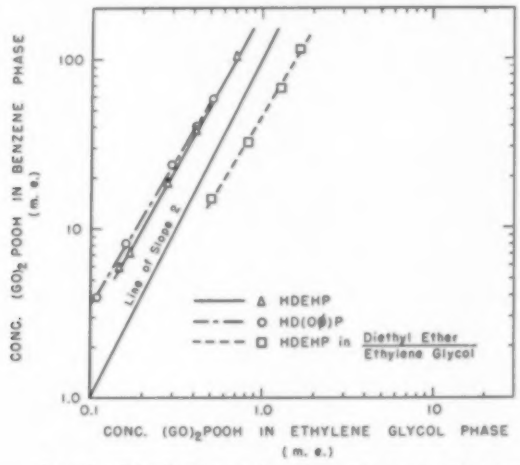


FIG. 2.—Distribution studies of monobasic phosphoric acids.

dimer, since it can form new hydrogen bonds with the phosphoric acids, much as the behaviour that acetic acid shows. The molecular weights of the monobasic acids are not water sensitive and so water in the ethylene glycol (0·7 per cent) should have no effect on the results.

The partition studies with mono-(2-ethylhexyl) phosphoric acid* were done in ethylene glycol containing 0·7% H_2O, and the results cannot be considered directly comparable because of the effect of water in increasing polymerization. Log-log plots of the acid concentration in benzene or diethyl ether vs. that in ethylene glycol gave straight lines with slopes of about 1·5.

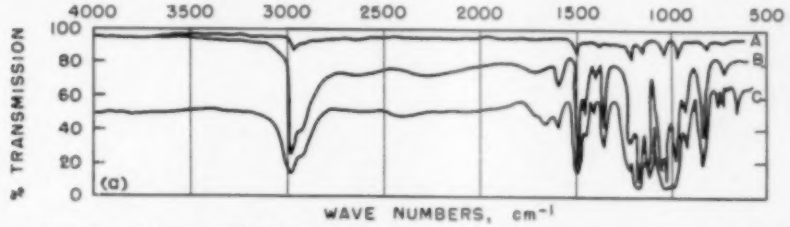
Infra-red studies

The infra-red spectra from 4000–650 cm^{-1} for several monobasic and dibasic phosphoric acids are shown in Figs. 3–5. These were obtained at various dilutions in CCl_4 and either as the KBr disk spectrum or as a liquid film spectrum. All of these spectra show the broad absorption of bonded OH in the region of 2700–2500 cm^{-1}. This region has been previously identified[32,33] as that of a bonded OH. We have confirmed this by deuteration of HDEHP. The deuterated HDEHP shows the peak in the 2700–2500 cm^{-1} region shifted toward lower frequencies. The phosphoryl absorption is that of a bonded P–O group. Even with dilution (1% CCl_4 solutions) no evidence of a free OH spectrum in the vicinity of 3500 cm^{-1} exists. The broad absorption spectrum of bonded OH remains. Dilute solutions in CCl_4 and dioxane fail to produce any free OH spectra even in the overtone region.

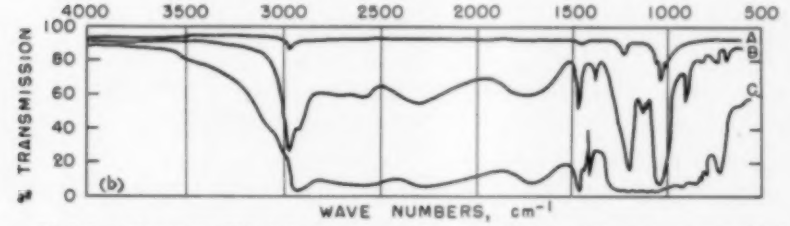
* Henceforth will be abbreviated as H_2MEHP.

[32] L. J. BELLAMY, *The Infra-red Spectra of Complex Molecules*. Wiley, New York (1954).
[33] L. W. DAASCH and D. C. SMITH, *Analyt. Chem.* **23**, 853 (1951).

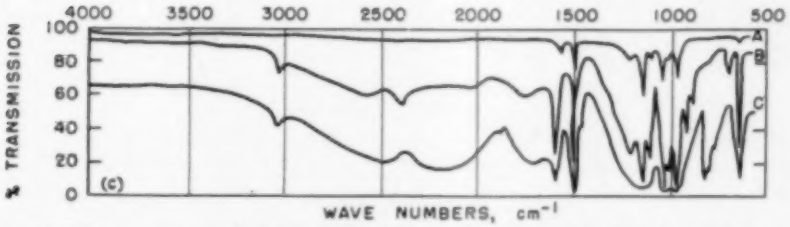
Fig. 6 shows the spectra of acetic acid (glacial) in the region of 4000–2500 cm^{-1}. Curve *B* illustrates the spectra of a 0·02 M solution of acetic acid in CCl_4 at 23° and 70°C. It is observed that at about 3550 cm^{-1} the free OH spectrum is intensified by heating. Fig. 7 shows the spectra of HDEHP in the region of 4000–2500 cm^{-1}. Curve *B* illustrates the spectra of a 0·03 M solution of this acid in CCl_4 at 23° and 70°C.



(a) Infra-red spectra of bis-[*p*-(1,1,3,3,-tetramethylbutyl) phenyl] phosphoric acid (0·025 mm cell.) *A*—1 per cent solution in CCl_4 vs. CCl_4; *B*—15 per cent solution in CCl_4 vs. CCl_4; *C*—KBr disk spectrum.



(b) Infra-red spectra of bis-(*n*-butyl) phosphoric acid (0·025 mm cell). *A*—1 per cent solution in CCl_4 vs. CCl_4; *B*—13 per cent solution in CCl_4 vs. CCl_4; *C*—liquid film spectrum.

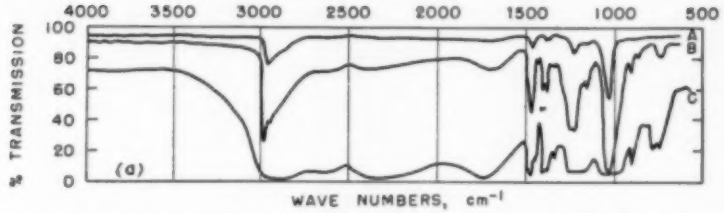


(c) Infra-red spectra of bis- (phenyl) phosphoric acid (0·025 mm cell). *A*—1·5 per cent solution in CCl_4 vs. CCl_4; *B*—10 per cent solution in CCl_4 vs. CCl_4; *C*—KBr disk spectrum.

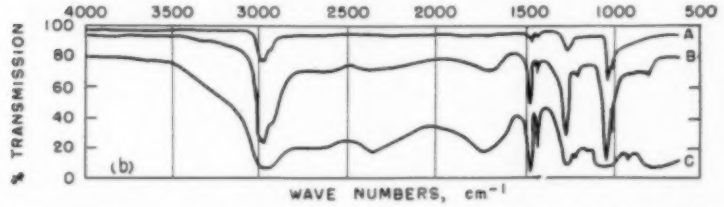
FIG. 3.—Infra-red spectra of several monobasic phosphoric acids.

Spectra at 23° and 70°C of 0·001 M solutions of HDEHP in CCl_4 (6 mm cell) were also investigated. The spectrum of free OH is not observed in any of these solutions. Curve *D* shows the spectra of the same acid in mineral oil at 23° and 133 ± 5°C. Again the spectrum of free OH is absent even at the higher temperature. Fig. 8 shows similar results with H_2MEHP. Dilutions with CCl_4 to 0·001 M in a 6 mm cell at temperatures up to 70°C fail to show a free OH spectrum. The insolubility of this acid in mineral oil precluded running the spectrum in this solvent.

The phosphoryl region (P → O) at 1225 cm^{-1} for pure HDEHP is also of interest. Since no free OH spectra have been observed it would be expected that the phosphoryl frequency would remain that of a bonded frequency, and would therefore not show

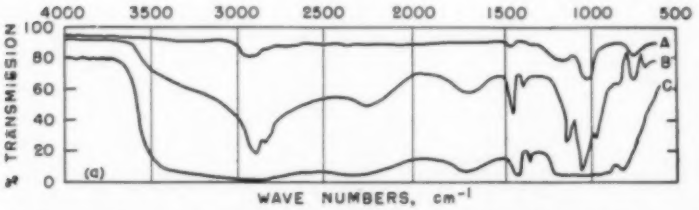


(a) Infra-red spectra of bis-(2,6,-dimethylheptyl-4) phosphoric acid (0·025 mm cell).
A—1·5 per cent solution in CCl_4 vs. CCl_4; *B*—12 per cent solution in CCl_4 vs. CCl_4; *C*—liquid film spectrum.

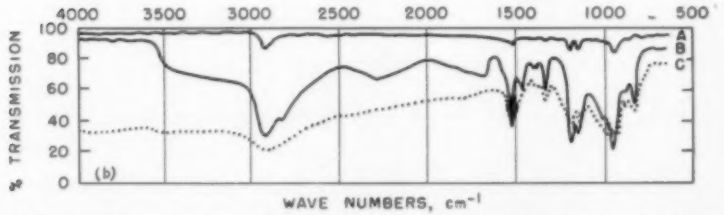


(b) Infra-red spectra of bis-(2-ethylhexyl) phosphoric acid (0·025 mm cell). *A*—1·4 per cent solution in CCl_4 vs. CCl_4; *B*—12 per cent solution in CCl_4 vs. CCl_4; *C*—liquid film spectrum.

FIG. 4.—Infra-red spectra of several monobasic phosphoric acids.



(a) Infra-red spectra of mono-(2-ethylhexyl) phosphoric acid (0·025 mm cell). *A*—1 per cent solution in CCl_4 vs. CCl_4; *B*—12 per cent solution in CCl_4 vs. CCl_4; *C*—90 per cent solution in CCl_4 vs. CCl_4.



(b) Infra-red spectra of mono-[*p*-(1,1,3,3,-tetramethylbutyl) phenyl] phosphoric acid (0·025 mm cell).
A—1 per cent solution in CCl_4 vs. CCl_4; *B*—10 per cent solution in CCl_4 vs. CCl_4; *C*—KBr disk spectrum.

FIG. 5.—Infra-red spectra of several dibasic phosphoric acids.

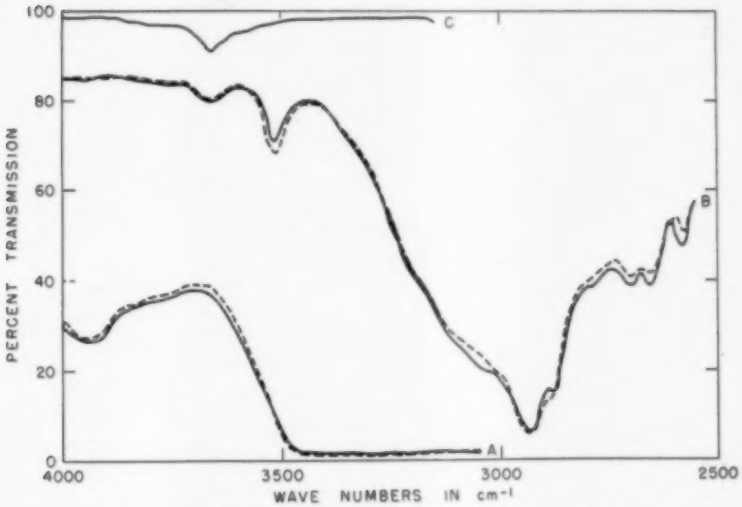


FIG. 6.—Infra-red absorption spectra of acetic acid (glacial).
A—liquid film vs. air at 23° and 100 ± 3°C (0·3 mm cell);
B—0·02 M solution in CCl_4 vs. air at 23° and 70 ± 3°C (6 mm cell);
C—liquid film CCl_4 vs. air at 23°C (6 mm cell).
——— room temperature experiments - - - - elevated temperature experiments

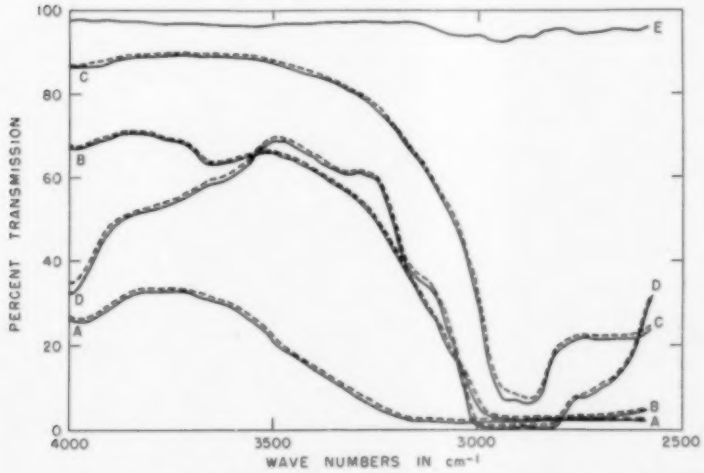


FIG. 7.—Infra-red absorption spectra of bis-(2-ethylhexyl) phosphoric acid.
A—liquid film vs. air at 23° and 120 ± 5°C (0·3 mm cell);
B—0·03 M solution in CCl_4 vs. air at 23° and 70 ± 3°C (6 mm cell);
C—0·03 M solution in CCl_4 at 23° and 70 ± 3°C (3 mm cell);
D—0·03 M solution in mineral oil vs. air at 23° and 133 ± 5°C (0·3 mm cell);
E—liquid film CCl_4 air at 23°C (3 mm cell).
——— room temperature experiments - - - - elevated temperature experiments

any change. Fig. 9 shows the spectra of this acid in a 1 per cent solution in mineral oil at 22° and 105°C. It is observed that no visible shift of the phosphoryl frequency has occurred.

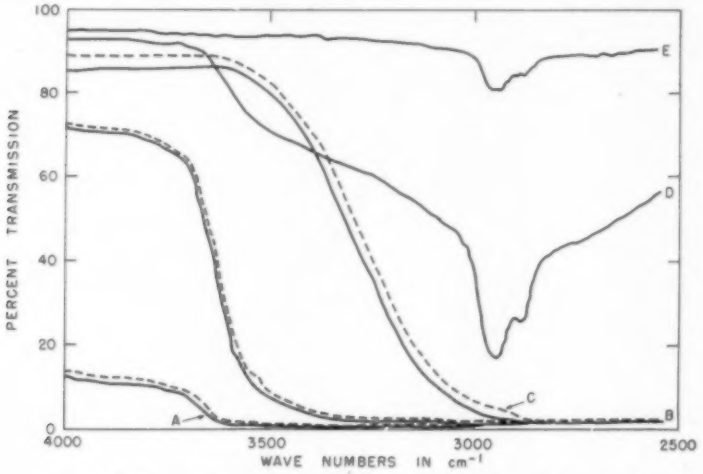


FIG. 8.—Infra-red absorption spectra of mono-(2-ethylhexyl) phosphoric acid.
A—liquid film vs. air at 23° and 140 ± 5°C (0·3 mm cell);
B—0·07M solution in CCl_4 VS·CCl_4 at 23° and 70 ± 3°C (3mm cell);
C—1 per cent solution in CCl_4 vs. CCl_4 at 25° and 70 ± 3°C (3 mm cell);
D—12 per cent solution in CCl_4 vs. CCl_4 at 23°C (0·025 mm cell);
E—1 per cent solution in CCl_4 vs. CCl_4 at 23°C (0·025 mm cell).
——— room temperature experiments – – – – elevated temperature experiments

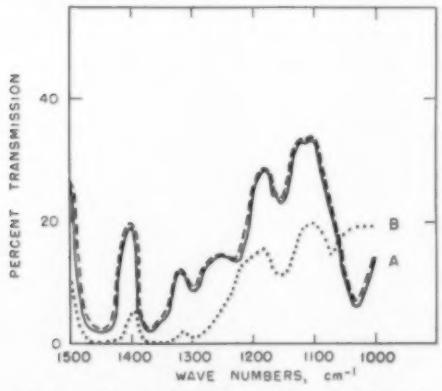


FIG. 9.—Infra red absorption spectra of bis-(2-ethylhexyl) phosphoric acid in mineral oil.
A—1 per cent solution of bis-(2-ethylhexyl) phosphoric acid in mineral oil vs. air at 22° and 105 ± 5°C (0·3 mm cell);
B—mineral oil liquid film vs. air at 22°C (0·3 mm cell).
——— room temperature experiments – – – – elevated temperature experiments

It thus appears that under similar experimental conditions where the monocarboxyl acids show the formation of free OH groups the monobasic and dibasic phosphoric acids fail to do so. Even under more drastic conditions (heating up to 135°C of the mineral oil solutions) the monobasic acids fail to produce free OH absorption spectra. Recently,[34] the infra-red spectrum of $(i\text{-}C_3H_7O)_2PO(OH)$ also failed to show a free OH

[34] J. W. MAARSEN, M. C. SMIT and J. MATZE, *Rec. Trav. Chim.* **76**, 713 (1957).

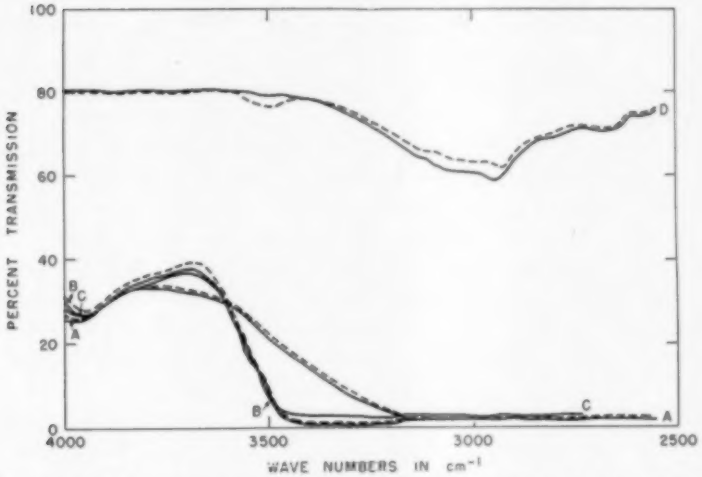


FIG. 10.—Infra-red absorption spectra of bis-(2-ethylhexyl) phosphoric acid, acetic acid and mixtures (0·3 mm cell).
A—liquid film of bis-(2-ethylhexyl) phosphoric acid vs. air at 23° and 120 ± 5°C;
B—liquid film acetic acid vs. air at 23° and 100 ± 3°C;
C—mole ratio acetic acid/bis-(2-ethylhexyl) phosphoric acid (65:1) vs. air at 23° and 100 ± 3°C;
D—0·02 M solution of acetic acid in CCl_4 vs. air at 22° and 70 ± 3°C.
——— room temperature experiments - - - - elevated temperature experiments

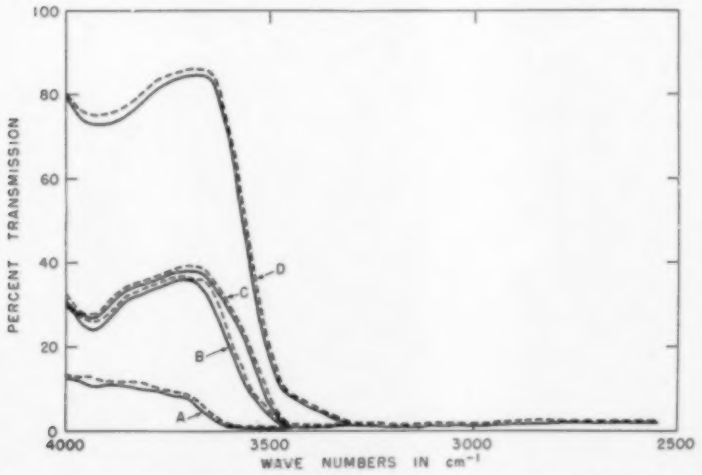


FIG. 11.—Infra-red absorption spectra of mono-(2-ethylhexyl) phosphoric acid, acetic acid and mixtures (0·3 mm cell).
A—liquid film of H_2MEHP vs. air at 23° and 140 ± 5°C;
B—mole ratio acetic acid/H_2MEHP (65:1) vs. air at 23° and 100 ± 3°C;
C—liquid film of acetic acid vs. air at 23° and 100 ± 3°C;
D—mole ratio acetic acid/H_2MEHP (65:1) vs. diaphragm cell at 26° and 100 ± 3°C.
——— room temperature experiments - - - - elevated temperature experiments

spectrum. It is thus believed that these acids are more strongly hydrogen bonded than are the monocarboxylic acids. DYRSSEN[35] has found that the dimerization constant of bis-(*n*-butyl) phosphoric acid is very large (3×10^4 in $CHCl_3$), and is probably larger in non-polar solvents. It is much larger than for any monocarboxylic acid. Thus this acid is probably predominately dimeric even in very low concentrations in non-polar solvents.

From the freezing-point studies it was observed that HDEHP and H_2MEHP showed monomeric molecular weights in acetic acid. In Fig. 10, Curve *C* shows the spectra of a solution of HDEHP in acetic acid at 23° and 100°C. The formal ratio of HDEHP to acetic acid is 1 : 65, precisely that used in the freezing-point measurement. At the two temperatures, no free OH spectra were observed. In Fig. 11, Curve *B* shows the spectra of a 65 : 1 (Acetic acid : H_2MEHP) mixture. Such a solution gave a monomeric molecular weight for H_2MEHP. Here again, at 23° and 100°C no free OH spectra could be seen. In view of the fact that monomeric molecular weights were obtained with HDEHP and H_2MEHP in acetic acid, and since no free OH spectra could be observed, the indications are that strong solute–solvent interactions have occurred. It is unlikely that the HDEHP and H_2MEHP have gone from intermolecular hydrogen bonded polymers to intramolecular hydrogen bonded monomers, since the presence of an excess of acetic acid capable of forming hydrogen bonds would very probably interact with these monomers as fast as they are formed.

From the cryoscopic studies, distribution studies, and infra-red work, it is believed that the monobasic and dibasic phosphoric acids form strong hydrogen bonds and thereby polymerize. Their hydrogen bonds are of a stronger nature than those present in monocarboxylic acids. The phosphoric acids are still to a very considerable degree polymerized under conditions where the monocarboxylic acids have monomerized to some extent.

Acknowledgements—The authors wish to thank Dr. J. V. QUAGLIANO and Brother C. CURRAN, C.S.C., of Notre Dame University for their many valuable suggestions and encouragement on the infra-red aspect of this work.

[35] D. DYRSSEN, *Acta Chem. Scand.* **11**, 1771 (1957).

J. Inorg. Nucl. Chem., 1958, Vol. 7, pp. 245 to 256. Pergamon Press Ltd., London

CORRELATION OF ABSORPTION SPECTRA AND PARTITION DATA FOR PLUTONYL NITRATE IN AQUEOUS AND ORGANIC MEDIA*

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(*Received* 6 *March* 1958)

Abstract—An examination of the absorption spectra of plutonyl nitrate in dibutyl carbitol shows the presence of two species, the dinitrate and the trinitrate, the latter being formed in the presence either of nitric acid or quaternary ammonium salts. The addition of tributyl phosphate to dibutyl carbitol solutions tends to suppress the trinitrate species.

The trinitrate has a much higher partition coefficient than the dinitrate for extraction into dibutyl carbitol from aqueous nitric acid and nitrates. This improvement in the organic extraction obtained by raising the aqueous acidity is shown, by correlation with absorption spectra, to be directly related to the production of the trinitratoplutonyl species from the dinitrate. The association constant for the reaction $PuO(NO_3)_2 + HNO_3 = HPuO_2(NO_3)_3$ in the organic solvent has been obtained with a value of 4 ± 1.

The relation of the plutonyl species present in the aqueous and organic phases is discussed.

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THIS work was initially begun in order to obtain partition data for hexavalent plutonium in concentrations of a milligram per ml for the systems aqueous nitric acid–dibutyl carbitol and aqueous nitric acid, ammonium nitrate–dibutyl carbitol. Dibutyl carbitol (DBC) is the dibutyl ether of di-ethylene glycol. These data have been obtained, and while following the absorption spectral behaviour, particularly in the organic phase, two species were observed, one at low and the other at high acidities. At about that time, work was published[1] on the dinitrato and trinitratouranyl species in a number of organic solvents. By analogy, the species in dibutyl carbitol were considered to be the di- and trinitrates of hexavalent plutonium.

EXPERIMENTAL

Purity of plutonium. The plutonium was purified by peroxide precipitation, and spectrographic analysis showed only trace quantities of impurities; of these the most prominent were iron (0·1 per cent) and uranium (1 per cent). The stock was kept as a concentrated solution of Pu(IV) (about 70 mg Pu/ml solution) in 6 M HNO_3.

Electrolytic oxidation of Pu(IV) *nitrate.* As the plutonium was required free from other inorganic materials, it was decided not to make use of the more usual oxidants such as silver peroxide or persulphate. Electrolytic oxidation was found to be elegant and simple and was used to prepare all the hexavalent plutonium required. The Pu(IV) stock was diluted to less than one normal in nitric acid and placed in the anode compartment of the electrolytic apparatus shown in Fig. 1. Quantities of plutonium used were from 2 to 20 mg/ml and 5 to 10 ml of solution altogether in the anode compartment. The nitric acid strength of the solution varied from 0·4 to 1 N. Because of the possibility of polymerization and precipitation of Pu(IV) the nitric acid concentration should be greater than 0·4 N and, as high nitric acid strength retards the oxidation, the acidity should not be greater than normal. Pure nitric acid of an equal normality was placed in the cathode compartment

* This work was carried out in 1951, and has only recently been declassified.

(1) L. KAPLAN, R. A. HILDEBRANDT and M. ADER, *J. Inorg. Nucl. Chem.* **2**, 153 (1956).

in sufficient quantity to keep the levels of the two liquids at the same height. Using a 120 V battery with a resistance and milliameter in the circuit, and passing a current of 10 mA the plutonium oxidized smoothly to the pink plutonium(VI) nitrate overnight. If too high a current is passed for too long, plutonium migrates to the cathode compartment and is there reduced by the evolved hydrogen in the presence of the platinum gauze to plutonium(III) nitrate. The oxidized plutonium was examined spectrophotometrically with a Unicam S.P.500 spectrophotometer, using the analytically important wavelengths[2] to ascertain the amounts of plutonium in the various valency states. On all occasions the oxidized solution was 99 $\pm$ 1% plutonyl nitrate.

Determination of plutonium. A 2π-geometry argon proportional-counter incorporating two scalers in series was used, enabling counts up to 200,000 per min to be made to 99 per cent accuracy without

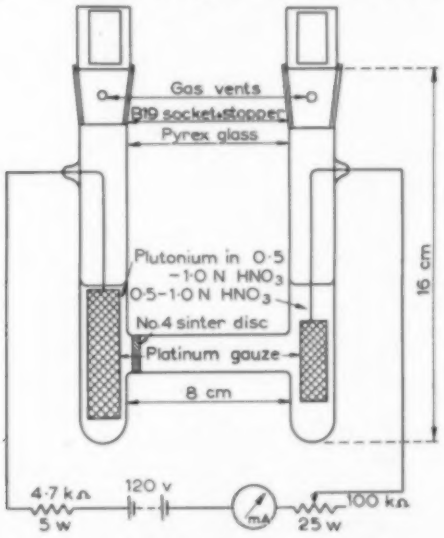


FIG. 1.—Electrolytic oxidation apparatus.

loss of counts. Ten or 25 μl aqueous samples were used directly on platinum discs for counts less than 200,000 per min. Otherwise they were washed into 5 ml flasks and aliquoted. 25 μl samples were taken direct from the organic phase into these 5 ml graduated flasks containing 0·2 N HNO_3 and shaken for a few minutes prior to direct mounting of 250 μl aliquots of the acid on platinum discs. Standard sources were used to relate the counts to the actual plutonium concentration.

Acidity determination. The 25 μl samples of the Pu solutions were titrated in a 1 ml beaker by dilute soldium hydroxide, stirring with CO_2-free air, using screened methyl orange indicator. The apparatus consists of a micrometer head firmly attached to a stainless steel plunger so no backlash is permitted, the plunger fitting into a glass syringe which is attached by standard glass joints to a capillary. The acid titrations are reproducible to $\pm$1 per cent. In the presence of NH_4NO_3, it was found that micro acidity determinations using screened methyl orange were very reproducible and agreed with macro determinations of nitric acid whether appreciable quantities of NH_4NO_3 were present or not. As an alternative to using an indicator similar determinations were made in the absence of NH_4NO_3 by conductimetric titration in a 1 ml beaker fitted with platinum black electrodes. The acidity of organic plutonium solutions were obtained by alcohol addition and titration to phenol phthalein end point or alternatively was read off from graphs obtained by titrating aqueous and organic phases on a macro scale in the absence of plutonium.

Solvents. Commercial DBC was refluxed with acid ferrous sulphate, washed and treated with alkaline permanganate until a permanent pink colour still persisted, the excess washed out and the carbitol thoroughly water-washed and finally distilled at 1–5 mm pressure. The constant boiling middle fraction was kept in a dark closed container in an inert atmosphere and the vessel then stored in

[2] M. KASHA, United States Atomic Energy Commission Unclassified Report MDDC 591 (1948).

solid carbon dioxide at −80°C. This DBC was only used up to a fortnight after distillation. Commercial tributyl phosphate was alkali and water washed then distilled at 140°C at 3 mm pressure.

Spectrographic measurements. The same unicam instrument was used throughout and all spectral measurements were made with a constant slit width of 0·010 mm in order to eliminate variable results particularly at the 830 μ plutonyl peak. Measurements were made in matched glass cells varying from 0·2 to 4·0 cm in path length, depending on the plutonium concentration. Blanks were prepared in both aqueous and organic phases using approximately the same composition but with plutonium absent.

Partitions. Plutonyl nitrate in aqueous solutions (3 to 5 ml) was added to an equal volume of "acid conditioned" dibutyl carbitol in a vessel comprising a 50 ml conical flask joined at the neck to the top of a graduated centrifuge tube at right angles. "Conditioned" organic solvent was obtained by three

TABLE 1.—SYSTEM H_2O–NH_4NO_3–HNO_3–$PuO_2(NO_3)_2$–DBC—VARYING HNO_3

Final aqueous phase acidity	0·02	0·03	0·06	0·22	0·26	0·33	0·44
$K_{Pu}\left(\frac{\text{organic}}{\text{aqueous}}\right)$	1·5	1·7	1·75	2·3	2·8	3·75	6·8
Final aqueous phase acidity	0·58	0·74	0·92	1·02	1·40	2·20	—
$K_{Pu}\left(\frac{\text{organic}}{\text{aqueous}}\right)$	10·2	15·4	19·3	21·8	24·3	24·6	—

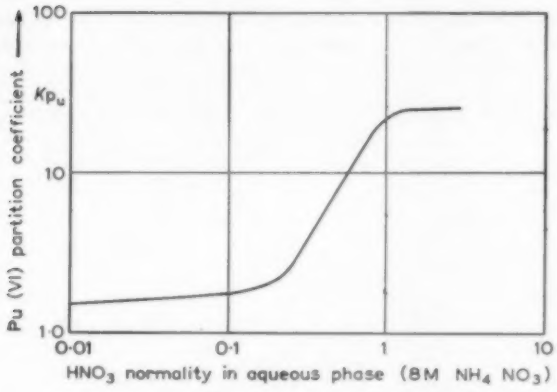
equilibrations of the solvent with equal volumes of aqueous nitric acid prior to the equilibration with the plutonyl nitrate of corresponding aqueous acidity. The ground glass stoppered flask was shaken mechanically for 15 min in a thermostat at 25°C, then rotated through 90° and the two phases poured into the centrifuge tube where they separated almost immediately. Samples were taken for (a) counting (b) acidity determinaton or (c) spectrographic study. In most cases plutonium was back extracted from the organic phase by its equilibration with two successive aqueous phases in order to check on the reproducibility of the partition coefficient which was usually within a few per cent.

Stability towards valency reduction of plutonyl nitrate. Electrolytically oxidized hexavalent plutonium nitrate was stable in nitric acid solution over a range of acidities from pH4 to 3 N in the concentration range 0·005 to 0·05 M Pu(VI), only 1 to 2 per cent of Pu(IV) and no Pu(V) or Pu(III) being detectable on standing for a period of about a week. The same stability was shown in the presence of up to 10 M ammonium nitrate. Nitrate solutions of hexavalent plutonium (0·025 M) to which ammonia was added to give solutions pH 4 to pH 7 were stable for several hours and we were unable to detect the formation of any Pu(V) or Pu(IV) using the usual spectrophotometric methods.[2] Hexavalent plutonium nitrate was also stable in the presence of purified DBC. Nitric acid solutions of plutonyl nitrate kept in the aqueous phase, in the organic phase or used for many equilibrations in and out of the aqueous and organic phases for a period of 10 days, still contained 99 ± 1 per cent of plutonium in the hexavalent state. In the above instances there was only pure DBC, HNO_3, and NH_4NO_3 present. On using commercial DBC the impurities in the solvent reduced Pu(VI) from 100 to 30 per cent when left overnight in contact with an aqueous phase. This figure did not change appreciably on standing a second night.

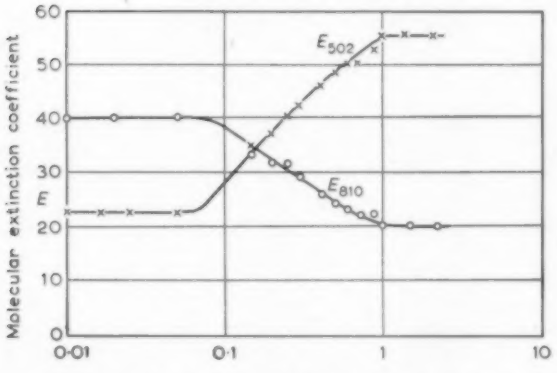
RESULTS AND DISCUSSION

Pu (VI) *partition data at* 25°C. A series of partition coefficients for plutonyl nitrate between 8 M NH_4NO_3 and DBC have been obtained at 25°C (Fig. 2a) over a range of 0·01 to 2·3 N HNO_3 in the aqueous phase, the plutonium concentration varying from 0·005 to 0·05 M, all as Pu(VI)

The partition of Pu(VI) between DBC and an aqueous solution of NH_4NO_3 of variable molarity with constant acidity at 25°C is shown in Table 2. The drop in K_{Pu} is greater at higher acidity partially owing to the decrease in the proportions of the species more soluble in the organic solvent as discussed later.



(a) Partition of Pu(VI) between aq. 8M NH_4NO_3 and DBC



(b) Height of Pu(VI) peaks at 502 and 810 mμ in DBC.

FIG. 2.—Extraction of Pu(VI) into DBC compared with absorption spectral peak heights

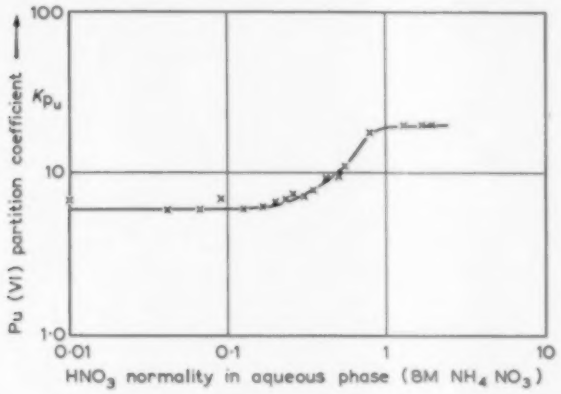
TABLE 2.—SYSTEM H_2O–NH_4NO_3–HNO_3–$PuO_2(NO_3)_2$–DBC—VARYING NH_4NO_3

Acidity 0·5 N HNO_3 NH_4NO_3 molarity	8·0	6·0	4·0	2·0	1·0	0·0
$K_{Pu}\left(\frac{\text{organic}}{\text{aqueous}}\right)$	1·8	0·96	0·41	0·10	0·042	0·0045
Acidity 1·5 N HNO_3 NH_4NO_3 molarity	8·0	6·0	4·0	2·0	0·0	—
$K_{Pu}\left(\frac{\text{organic}}{\text{aqueous}}\right)$	24·5	10·4	4·5	0·64	0·13	—

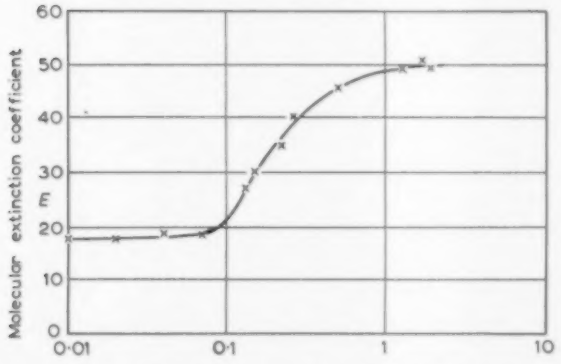
Similar partition data at 25°C were obtained (Fig. 3a) using a mixed solvent 97% DBC and 3% TBP and 8MNH_4NO_3

Partition data were also obtained at 25°C between DBC and aqueous HNO_3 in the absence of NH_4NO_3 at plutonium concentrations from 0·05 to 0·005 M.

Absorption spectra of DBC *solutions of* Pu(VI). An examination of the absorption



(a) Partition between 8MNH_4NO_3 and 3% TBP–DBC



(b) Height of Pu(VI) peak at 502 mμ in 3% TBP–DBC.

FIG. 3.—Extraction of Pu(VI) into 3% TBP–DBC compared with absorption spectral peak heights

spectra of the organic phases produced in the above partition work showed quite clearly that there were two species present. At low acidities (<0·07N HNO_3 in the organic solution) the 502 mμ peak is at its lowest (E, the molar extinction coefficient = 22) and the 810 mμ peak is at its highest ($E_{810} = 40$). As the organic phase acidity is increased so the 502 mμ peak rises and the 810 mμ peak falls until at an organic acidity of 1·3 $E_{502} = 56$ and $E_{810} = 20$. Further acidity increase does not appreciably affect these maximum and minimal heights. These spectra demonstrate the presence of two species at the low and high acidities with a mixture of the two species at intermediate acidities (Fig. 4). It is noteworthy that whether the DBC–Pu solution is obtained from partition with an aqueous solution of HNO_3 alone or an aqueous solution of HNO_3 plus NH_4NO_3 it will have a definite Pu spectrum depending only on

the HNO_3 concentration of the DBC solution itself. It is obvious from a comparison of the partition curves with the spectral peaks showing the change of species (Fig. 2 and 3) that the complex produced at the higher acidities in the DBC is the much more extractable species. This latter species was obtained in DBC of low HNO_3 concentration by addition of solid tetra-butyl-ammonium nitrate and heptyl-pyridinium nitrate to dibutyl-carbitol solutions of Pu(VI) when the value of the extinction coefficients at 502 mμ was changed from 22 to 56. This is shown below in the nearly quantitative effect of the addition of one equivalent of tetra-butyl-ammonium nitrate to a 0·0085

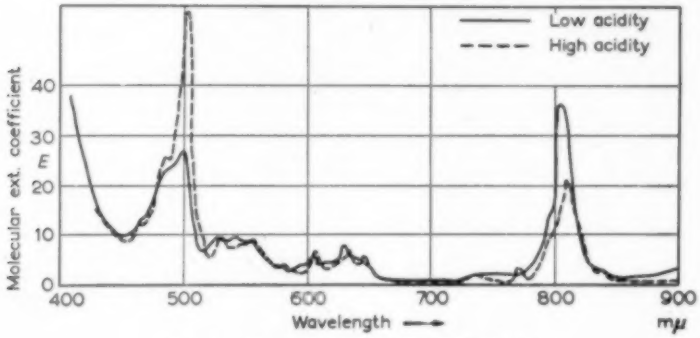


FIG. 4.—Absorption spectra of Pu(VI) in DBC.

molar solution of $PuO_2(NO_3)_2$ in DBC of very low acidity ($< 0{\cdot}02$ N). α is the fraction more complexed.

Re-equilibration of this organic phase with an equal volume of the original aqueous phase, after the above addition of quaternary salt 0·017 M in the organic solvent, produced an improvement in the Pu partition coefficient from 1·4 to 4·6.

Both HNO_3 and quaternary ammonium nitrate change the species in the same way but the latter has a much greater complexing power. The fact that the Pu(VI) in the organic solvent is nearly completely changed from the assumed dinitrate to the trinitrate after a 1:1 addition of the quaternary salt is good evidence that a 1:1 complex is formed according to the reaction $PuO_2(NO_3)_2 + RNO_3 \rightleftharpoons R\ PuO_2(NO_3)_3$. This is very similar to the production of the trinitratouranyl nitrate reported by KAPLAN *et al.*[1] by addition of quaternary ammonium salts to organic solutions of the neutral uranyl dinitrate. These workers have produced the corresponding trinitratouranyl species in ketones using stoicheiometric quantities of tetra-butyl-ammonium nitrate, but the inorganic solutions were made up from the solid materials and dry solvent. The presence of water inhibited the reaction somewhat. The heptyl-pyridinium nitrate produced only 88 per cent complexing, which KAPLAN attributed to its relatively inferior ionization in ketones. It was also found that ethers required much higher concentrations of substituted ammonium nitrate than ketones to produce the same degree of complexing to the trinitrate form. In fact, KAPLAN *et al.* were unable to obtain the trinitratouranyl species in DBC. The present authors did obtain the typical trinitratouranyl nitrate absorption spectra in purified DBC by using an excess of quaternary ammonium nitrate.

Nitric acid causes complex formation of Pu(VI) to a much less degree than quaternary ammonium salts. The degree of complexing of 0·008 M Pu in a nitric acid

TABLE 3.—SYSTEM H_2O–NH_4NO_3–$PuO_2(NO_3)_2$–DBC–TBP—VARYING HNO_3

Final aqueous phase acidity	0·01	0·02	0·037	0·067	0·133	0·175	0·235
$K_{Pu}\left(\frac{\text{organic}}{\text{aqueous}}\right)$	7·2	8·5	5·7	5·9	6·1	6·2	6·4
Final aqueous phase acidity	0·32	0·42	0·56	0·77	1·3	1·67	1·88
$K_{Pu}\left(\frac{\text{organic}}{\text{aqueous}}\right)$	7·4	9·0	10·7	17·2	18·7	19·3	19·5

TABLE 4.—SYSTEM H_2O–HNO_3–$PuO_2(NO_3)_2$–DBC—VARYING HNO_3

HNO_3 acidity aqueous	9·0	8·7	7·2	6·0	5·3	3·8	3·1
HNO_3 acidity organic	4·9	4·75	3·9	3·3	2·86	1·96	1·45
$K_{Pu}\left(\frac{\text{organic}}{\text{aqueous}}\right)$	5·4	7·8	9·2	6·2	5·0	3·6	1·8
HNO_3 acidity aqueous	2·05	1·37	0·85	0·45	0·15	0·010	—
HNO_3 acidity organic	0·64	0·26	0·095	0·015	0·002	0·001	—
$K_{Pu}\left(\frac{\text{organic}}{\text{aqueous}}\right)$	0·43	0·11	0·025	0·010	0·0045	0·0040	— >

TABLE 5.—EFFECT OF QUATERNARY AMMONIUM SALTS ON DBC SOLUTIONS OF Pu(VI)

$\frac{\text{Molarity of } R_4N\,NO_3}{\text{Molarity of } PuO_2(NO_3)_2}$	0	0·5	1·0	1·5	2·0
E(502 mμ)	22	35	47	51	56
α	0	0·38	0·74	0·86	1·0

concentration of 0·6 M in DBC is only the same as that of 0·008 M $R_4N{\cdot}NO_3$ in DBC. The association constant K for the assumed reactions $PuO_2(NO_3)_2 + HNO_3 \rightleftharpoons HPuO_2(NO_3)_3$ is calculated from $K = \alpha/(1-\alpha)\ 1/HNO_3$ where α is the fraction of plutonium complexed. This value of K is only a "mass action" association constant as no account is taken of activity coefficients in the calculations. The heights of the 502 mμ peak and the 810 mμ peak at $\alpha = 0$ are taken as 22 and 40 respectively. Similarly at $\alpha = 1$ they are 56 and 20. Points along the lines of Fig. 2 indicate the degree of complexing at the appropriate HNO_3 acidity and are compared with the partition coefficients of Pu(VI) showing the increasing extraction due to the formation of the more extractable trinitratoplutonyl species. Tables 6 and 7 contain the values of the association constant K primarily for solutions that have been in equilibrium with 8 M NH_4NO_3 solution at 25°C. There are also included, for comparative purposes, values of K obtained from DBC in equilibrium with 10 M NH_4NO_3 and with HNO_3 in the absence of NH_4NO_3.

These figures give a mean value for the "mass action" association constant of 4 ± 1.

The effect of nitric acid on complexing Pu(VI) in the DBC–TBP mixture is shown in Fig. 4 by the gradual increase in the 502 mμ spectral peak from $E = 18$ to $E = 50$.

TABLE 6.—COMPLEXING EFFECT OF HNO_3 ON Pu(VI) IN DBC, BASED ON 502 mμ SPECTRAL PEAK

HNO_3 acidity		E	α	K
Aq.	Organic			
8 M NH_4NO_3 in aqueous phase				
0·05	0·06	22	0·0	—
0·09	0·10	31·5	0·28	3·9
0·15	0·17	34	0·36	3·3
0·20	0·25	37·5	0·45	3·4
0·25	0·30	40	0·53	3·8
0·30	0·40	42	0·59	3·6
0·42	0·55	46	0·71	4·4
0·50	0·69	48	0·76	4·7
0·60	0·84	50	0·82	5·5
0·74	0·96	50	0·82	4·8
0·91	1·18	51	0·85	4·9
1·00	1·36	56	1·00	—
10 M NH_4NO_3 in aqueous phase				
0·16	0·27	41	0·56	4·7
No NH_4NO_3 in aqueous phase				
1·35	0·25	35·5	0·37	2·7
1·70	0·40	42	0·59	3·6
2·10	0·64	47	0·74	4·4
2·50	1·00	50·5	0·84	5·1

Together with causing changes in the spectral peak heights, the 3% TBP also causes the amount of trinitrato species in the DBC to decrease. This is because TBP forms a stronger dinitrate complex with both uranyl and plutonyl nitrates than DBC does. In fact, the absorption spectra of both uranyl and plutonyl nitrates in TBP or TBP plus inert diluents do not change at high or low acidities and also remain the same in the presence or absence of quaternary ammonium nitrates. The Pu(VI) spectrum in TBP plus inert diluent is very similar to that of Pu(VI) in DBC at very low acidities, and is probably the spectrum of the neutral dinitrate. The TBP competes with nitric acid for the plutonium and at low acidities extracts more Pu(VI) from aqueous solution than at high acidities, so a TBP trinitrato-plutonyl complex cannot be formed. This behaviour is analogous to that of the TBP–uranyl system.

Comparison of aqueous and organic $PuO_2(NO_3)_2$ *spectra.* In order to obtain the least complexed aqueous solution of plutonyl nitrate an absorption spectrum was obtained

of an electrolytically oxidized solution diluted to 0·02 N in HNO_3 (Fig. 5). This spectrum does not differ appreciably either from the spectrum in normal perchloric acid or in normal nitric acid. As it is known[3] that the absorption spectrum of plutonyl perchlorate remains uncomplexed from pH 3 to 9 N, the absorption spectrum of plutonyl nitrate from 0·02 to 1 N is assumed to be that of the uncomplexed plutonyl species (PuO_2^{++}). The vibrational fine structure attributed by KASHA[2] to the O–Pu–O

TABLE 7.—COMPLEXING EFFECT OF HNO_3 ON Pu(VI) IN DBC, BASED ON 810 mμ SPECTRAL PEAK

HNO_3 acidity		E	α	K
Aq.	Organic			
8 M NH_4NO_3 in aqueous phase				
0·05	0·06	40	0·0	—
0·09	0·10	34·5	0·28	3·8
0·15	0·17	32	0·40	3·9
0·20	0·25	31	0·45	3·3
0·25	0·30	31	0·45	2·7
0·30	0·40	29	0·54	2·9
0·42	0·55	27	0·65	3·4
0·50	0·69	24·5	0·77	4·9
0·60	0·84	23·5	0·83	5·6
0·74	0·96	23·5	0·83	4·9
0·91	1·18	23	0·85	4·8
1·00	1·36	20	1·00	—
10 M NH_4NO_3 in aqueous phase				
0·16	0·26	30·7	0·46	3·4
No NH_4NO_3 in aqueous phase				
1·35	0·25	31	0·54	2·9
1·7	0·40	28	0·60	3·8
2·1	0·64	26	0·70	3·6
2·5	1·00	23·5	0·83	4·7

vibration is not too well defined in 0·02 N HNO_3 and not so sharp as in 0·1 N HNO_4.[4] Starting with the 3940 Å band of PuO_2^{++} successive frequency intervals of 656, 680 and 671 cm^{-1} are found giving a mean value of 670 cm^{-1} in fair agreement with CONNICK's figure[4] of 707 cm^{-1}.

Addition of ammonia to 0·02 N HNO_3 solution of Pu(VI) causes a new spectral peak to appear at 843 mμ at pH higher than 4 which gradually increases while the 828 mμ

[3] J. C. HINDMAN, AECD 1893 (1948).
[4] R. E. CONNICK, M. KASHA, W. H. MCVEY and G. E. SHELINE, United States Atomic Energy Commission Unclassified Report MDDC 892, (1948).

plutonyl peak decreases in height (Fig. 5). The variation with pH of both peak heights and of colour is shown in Table 8, *d* being the optical density.

Above pH-4 several hydrolytic reactions occur,[5] but at lower pH the absorption spectrum is that of the unhydrolysed plutonyl nitrate and hence all the partition and

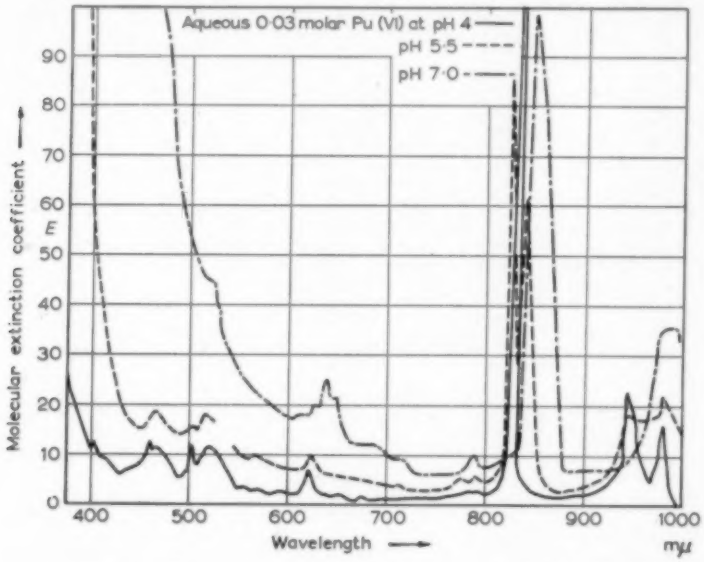


FIG. 5.—Absorption spectra of Pu(VI) in aqueous solution pH 4 to 7.

spectral investigations in the present work with organic extractions are carried out with unhydrolysed plutonyl species. From pH = 4 to 2 N HNO_3 there is little apparent change in the spectrum indicating that the PuO_2^{++} species alone is in solution. Increase in acidity above 2 N causes a change in colour from pink to pink-yellow and a very gradual decrease in the 828 mμ peak height (characteristic peak of the PuO_2^{++} species). Above 3 N HNO_3 (yellow solution) (Fig. 6) a small absorption band appears at 815 mμ

TABLE 8.—EFFECT OF pH CHANGE ON Pu(VI) ABSORPTION SPECTRUM

	pH1	pH4			NH_4OH			pH7	
	d	*d*	*d*	*d*	*d*	*d*	*d*	*d*	*d*
828 mμ	1·46	1·45	1·25	1·19	1·10	1·04	0·75	0·65	0·54
845 mμ	0·054	0·056	0·91	1·46	1·50	1·68	1·71	1·80	2·4
Colour	pink	pink	pink-yellow		deep-yellow		orange-yellow		

and at 11 to 15 N acid the 815 mμ band has greatly increased in height while the 828 mμ peak is gradually eliminated. At the same time, above 6 N HNO_3 a peak gradually rises at 480 mμ. Assuming that PuO_2^{++} is present at low acidities, then above 2 N HNO_3 the $PuO_2(NO_3)^+$ species may appear followed by the dinitrate

[5] L. E. MOORE and K. A. KRAUS, United States Atomic Energy Commission Unclassified Report MDDC 1105, (1949).

$PuO_2(NO_3)_2$ and possibly the trinitrate $PuO_2(NO_3)_3^-$. In uranium aqueous acid solutions no trinitrate occurs, although the other species are reported.[1] Evidence for a negatively charged plutonyl species is given by[6] electrical transference data. Addition of NH_4NO_3 to nitric acid solutions of Pu(VI) increases the plutonium complexing.

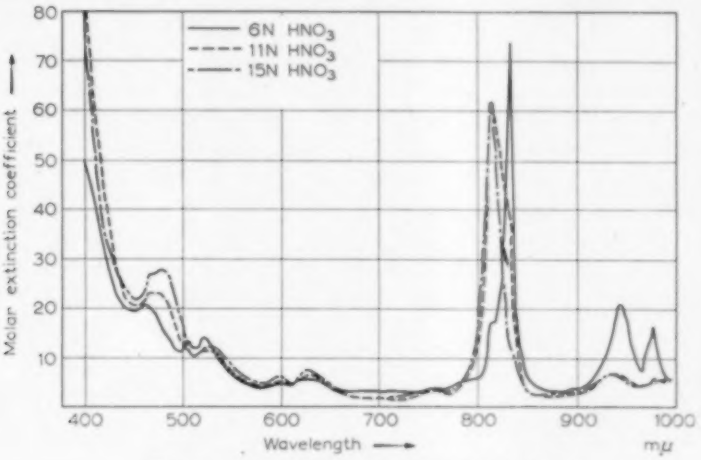


FIG. 6.—Absorption spectra of Pu(VI) in nitric acid.

TABLE 9.—Pu(VI) SPECIES IN ORGANIC PHASE AT EQUILIBRIUM WITH VARYING AQUEOUS PHASES

Aqueous phase	Organic phase				
	Solvent	HNO_3 conc.	Probable Pu species	Spectrum peak heights	
				502 mμ	810 mμ
No NH_4NO_3 < 0·8 N HNO_3	DBC	<0·09 N	dinitrate	22	40
0·8–3 N	DBC	0·9 to 1·4 N	dinitrate plus trinitrate	22–56	20–40
3–6 N	DBC	1·4 to 3·2 N	trinitrate	56	20
<6 N	DBC	>3·2 N	more complexed than trinitrate	42 (496 mμ)	20 (805 mμ)
8 M NH_4NO_3 < 0·1 N HNO_3	DBC	<0·09	dinitrate	22	40
0·1 to 0·9 N	DBC	0·9 to 1·2 N	mixed dinitrate and trinitrate	22–56	20–40
0·9 to 2·2 N	DBC	1·2 to 2·6 N	trinitrate	56	20
0·07 N	3%TBP –DBC	0·07 N	dinitrate	18	38

The absorption spectrum in 0·06 N HNO_3, 8 M NH_4NO_3 is very similar to the spectrum in 2 to 3 normal HNO_3 alone, while the spectra in 2 N HNO_3, 8 M NH_4NO_3 and 4 to 5 N HNO_3 are also similar to each other. It is probable that there is

[6] C. K. MCLANE J. S. DIXON and J. C. HINDMAN, *The Transuranium Elements* (Edited by G. T. SEABORG, J. J. KATZ and W. M. MANNING) NNES Plutonium Project Record, Div. IV, Vol. 14B, p. 358. McGraw-Hill, New York (1951).

complexing either to the PuO_2^+ or neutral $PuO_2(NO_3)_2$ species, but unlikely that there is any appreciable amounts of trinitrate form present in the NH_4NO_3 solutions.

A comparison of the absorption spectra of dilute aqueous HNO_3 solutions of Pu(VI) with those in DBC or DBC–TBP solutions shows very little in common. However, strong aqueous HNO_3 solutions (11–15 N) have spectra very similar to that of the neutral dinitrate in DBC, but this is not in agreement with electrical transference measurements which suggest a negatively charged species in strong HNO_3. From these transference measurements, one would expect Pu(VI) absorption spectra in strong HNO_3 similar to the trinitrate species in DBC but this is not the case. The table below shows the aqueous and organic acidities in equilibrium and the different Pu(VI) species present in the organic phase.

It is seen that the organic phase in equilibrium with 3–6 N aqueous HNO_3 contains primarily the trinitrate plutonyl species but above 6 N aqueous HNO_3 the species in DBC is even more complexed. This does not resolve the problem of the species in strong aqueous HNO_3 as the di- or trinitrate species in the aqueous phase could be in equilibrium with a different organic species. Further work, preferably non-spectrophotometric work, is needed to clarify the position of the Pu(VI) species in aqueous nitric acid before any real correlation with the organic solutions can be made.

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STUDIES ON PROTACTINIUM(V) IN NITRIC ACID SOLUTIONS

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Abstract—Reproducible solutions less than 10^{-4} M in protactinium-231 in 1–12 M nitric acid have been prepared and examined. Extraction of Pa by tributylphosphate resembles that of zirconium and equilibrium is rapidly attained. The relative strengths of fluoro-complexing of Pa(V) and Th(IV) in nitric acid have been derived by similar extraction experiments. Distribution coefficients using butex, solutions of tri-*n*-octylamine and di(2-ethylhexyl) phosphoric acid in inert organic diluents, and cation and anion exchange resins have also been measured. The protactinium species in nitric acid are interpreted as a series of hydroxo-nitrato complexes.

The adsorption of protactinium from these solutions on active solids and a comparison of thorium, uranium and protactinium exchange on ZeoKarb 225 and DeAcidite FF is also reported.

THE behaviour of protactinium towards solvent extraction, ion-exchange, and adsorption from nitric acid solution is of interest since (i) protactinium-233 is produced in irradiated thorium and it may be necessary to process it in future reactors working on the thorium-232 and uranium-233 cycle, and (ii) comparatively little is known about the structure of protactinium species in nitric acid solution.

A review of references up to 1951 on the solvent extraction and adsorption of protactinium has been given by ELSON.[1] Solvent extraction from HCl and HNO_3 solutions has more recently been reviewed by GOBLE *et al.*[2] who at the same time reported work on the amyl acetate–nitric acid system in which they found that the nature of the extracting complex changed with time. The extraction of protactinium-233 by di*iso*propylketone from nitric acid and nitrate solutions has been studied in detail by HYDE *et al.*[3]

FLETCHER and REES[4] have described experiments on the extraction of protactinium-233 by tributylphosphate (TBP) from nitric acid solution. Their work has been extended and detailed results are presented below on the solvent extraction and ion-exchange of protactinium-231, and on adsorption upon adsorbent solids, from nitric acid solution. The extraction and ion-exchange of protactinium is also compared with the behaviour of uranium and thorium under similar conditions.

PART I—THE SOLVENT EXTRACTION OF PROTACTINIUM-231

Experimental

Preparation of solutions of protactinium in nitric acid

Mg amounts of protactinium-231 were available in a HCl–HF solution at a concentration of 0·3 mg Pa/ml. From this, stock solutions (of the order of 10^{-3}–10^{-4} M protactinium in 6 M HNO_3) were prepared by evaporating almost to dryness with nitric acid several times, followed by three

(1) R. E. ELSON, *National Nuclear Energy Series* Vol. 14A, Chap. V, pp. 103–129. McGraw-Hill, New York (1954).
(2) A. GOBLE, J. GOLDEN and A. J. MADDOCK, *Canad. J. Chem.* **34**, 284 (1956).
(3) E. K. HYDE, *et al.*, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1955. Vol. 7, p. 281. United Nations (1956).
(4) J. M. FLETCHER and D. REES, *AERE/C/M*–236 (1954).

precipitations by ammonium hydroxide, to assist in the decontamination from fluoride, with resolution each time in cold 6 M HNO_3. It was found necessary to dissolve the hydroxide precipitate shortly (<5 min) after its formation to prevent ageing to nitric acid-insoluble compounds of protactinium. The solutions so prepared always contained small amounts of α-activity (~5 per cent of the total) inextractable by TBP. Prolonged centrifuging and heating to 100°C in sealed tubes reduced the α-active inextractable material to 1 per cent: this was due to daughters of protactinium-231. Aqueous stock solutions were obtained free from inextractable α-activity by a preliminary solvent extraction cycle, e.g.: by extraction from 10 M HNO_3 for 2 min with 50% TBP, stripping with 2 M HNO_3, and scrubbing the nitric acid solution with benzene to remove traces of TBP.

Preparation of solvents

Commercial TBP was steam-stripped from N/10 alkali, washed, dried, and stored in the dark. It was diluted with odourless kerosene and freshly conditioned before use by stirring three times with an equal volume of nitric acid of the required concentration.

Commercial butex (the dibutyl ether of diethylene glycol) was refluxed for 1 hr with acid ferrous sulphate solution and the separated organic layer washed with alkaline potassium permanganate solution until the pink colour remained unchanged after 2 hr. After filtration to remove the solid residue, the organic phase was washed with sodium metabisulphite solution, then with water, and finally distilled under vacuum at a pressure not exceeding 3 mm Hg. It was stored in a dark bottle, since peroxides form on warming and on exposure to light.

Dibutylphosphoric acid was isolated from a commercial mixture of mono- and di-butylphosphoric acids (supplied by Messrs. Albright and Wilson, Ltd., London) by solvent extraction with dibutylether.[5] Di(2-ethylhexyl) phosphoric acid was supplied by Chemical Research Laboratories, Teddington, and had been purified by a similar solvent extraction method.

Tri-*n*-octylamine was supplied by The British Hydrological Corporation, High Path, Merton, London. It gave no test for primary or secondary amines and was used without further purification.

Determination of distribution coefficients

The concentration of protactinium in aqueous and organic solutions was determined by α-counting on platinum or stainless steel trays, and the amount of α-active daughters was determined by α-pulse analysis.

Forward distribution coefficients, D_{Pa} (organic/aqueous), from aqueous solution, were determined on the stock solutions diluted where necessary to adjust the protactinium concentration. Strip distribution coefficients, *strip* D_{Pa}, were determined from solvents freshly loaded with protactinium.

Solvent extraction was carried out in "aged" polythene tubes with equal volume phases (except where otherwise stated) stirred for 2 min at approximately 20°C. "Aged" polythene apparatus, i.e. apparatus which had been treated several times with the solvent, was used because in new apparatus D_{Pa} increases with stirring time due to some impurity in the polythene dissolving in the solvent phase. D_{Pa} is independent of stirring time above about 1 min in glass apparatus and in "aged" polythene apparatus. The increase of D_{Pa} with stirring time in new apparatus is greater at 50°C than at 20°C and has been shown not to be due to dibutylphosphate which may arise from acid-hydrolysis of TBP during long times of stirring.

The effect of long equilibration time reported by GOBLE *et al.*[2] in the amyl acetate/HNO_3 system may be explained by the presence of small amounts of impurities, e.g. plasticizers, extracted from the polythene by the solvent. PEPPARD *et al.*[6] have made a similar suggestion to explain the large differences that GOLDEN and MADDOCK[7] found between protactinium extraction in glass and in polythene apparatus in the HCl-di*iso*propylketone system.

Solvent Extraction by TBP

In the following experiments the protactinium is considered to be in the (V) valency state. No significant variation in D_{Pa} was found for TBP extractions of a 10^{-5} M protactinium solution in 10 M HNO_3 after treatment for 1 hr at 90°C with (i) hydrazine

[5] D. C. STEWART and H. W. CRANDALL, *J. Amer. Chem. Soc.* **73**, 1377 (1951).
[6] D. F. PEPPARD, G. W. MASON and M. V. GERGEL, *J. Inorg. Nucl. Chem.* **3**, 370 (1957).
[7] J. GOLDEN and A. G. MADDOCK, *J. Inorg. Nucl. Chem.* **2**, 46 (1956).

nitrate, and (ii) sodium bromate, i.e. there is no indication of a change in the valency state of protactinium under these conditions.

The determination of the proportion of TBP-*inextractable protactinium*

The proportion of TBP-inextractable protactinium in a given aqueous solution was determined by extractions with 30 per cent TBP by the MARTIN technique,[8] i.e. with varying ratios of solvent phase volume to aqueous phase volume. The concentration of the protactinium in the organic phase was plotted as ordinate against the concentration of protactinium in the aqueous phase as abscissa. For a solution containing a number of extractable species in rapid equilibrium a straight line is obtained which passes through the origin. For a solution containing extractable species in equilibrium together with one (or more) inextractable species not in rapid equilibrium a straight line cutting the abscissa is obtained, the intercept giving the proportion of inextractable material, and the slope of the line the distribution coefficient of the extractable species. Fig. 1 gives the plot for a solution about 10^{-5} M in protactinium in 6 M HNO_3 extracted at ratios of solvent phase volume to aqueous phase volume of 0·15 to 10. This indicates that approx. 5 per cent of the protactinium is TBP-inextractable and for the other 95 per cent, $D_{Pa} = 2{\cdot}2$. Other solutions of about the same order of protactinium concentration examined by this technique gave a proportion of inextractable material ranging from 5 per cent to 20 per cent, and D_{Pa} from 2·2 to 3·0.

Variation of D_{Pa} *with the concentration of* HNO_3 *and of* TBP

A series of solutions of 10^{-5} M protactinium in 1–12 M HNO_3 was prepared from a centrifuged stock solution of 10^{-4} M protactinium in 6 M HNO_3 and aged for 5 days before use. A determination of the distribution of protactinium into 30 per cent TBP from the 6 M HNO_3 solution by the MARTIN technique indicated 8 per cent inextractable protactinium and 92 per cent with $D_{Pa} = 3{\cdot}0$. Values of D_{Pa} for forward extraction into 1–30 per cent TBP and for stripping from the 5 and 30 per cent TBP phases are plotted in Fig. 2. The small difference between the forward D_{Pa} and *strip* D_{Pa} for otherwise identical conditions is due to the 8 per cent of TBP-inextractable protactinium in the original stock solution.

Straight-line plots of mean slope 2·0 for log [TBP] vs. log D_{Pa} (Fig. 3) indicate that two molecules of TBP are associated with each molecule of protactinium extracted over the range 1–12 M HNO_3.

Rate of attainment of equilibrium in HNO_3 *solutions*

In the majority of the metal nitrate systems examined by solvent extraction with TBP the nitrato-complexes involved are mononuclear and labile, and distribution coefficients for their aqueous solutions are independent of the manner in which particular solutions are formed and their ageing time. Similar experiments with protactinium show that equilibrium between the nitrato complexes is rapidly attained.

10^{-5} M protactinium solutions were adjusted to 6 M HNO_3 and D_{Pa} was determined after varying lengths of time. The value (2·2) of D_{Pa} into 30 per cent TBP was independent of ageing time (2 min to 24 hr) and of the HNO_3 concentration of the initial protactinium solution.

[8] F. S. MARTIN, *AERE/C/R*–816 (1951).

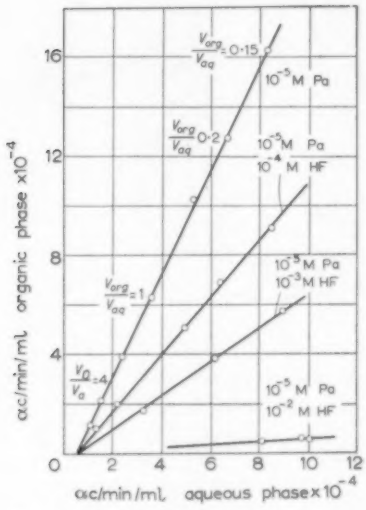

FIG. 1.—(i) Determination of the proportion of TBP-inextractable protactinium in a nitric acid solution, and (ii) the effect of HF on the extraction of protactinium.

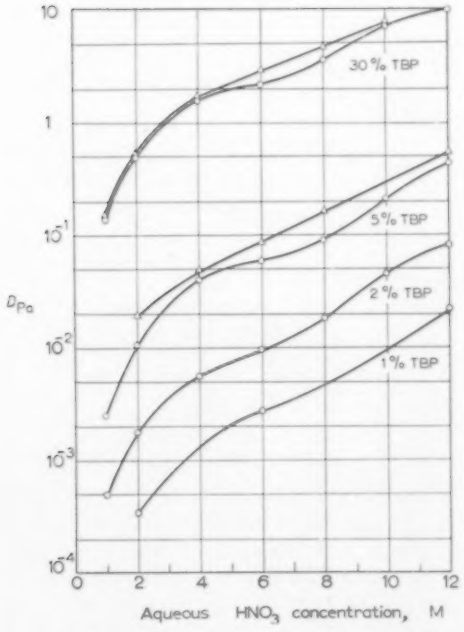

FIG. 2.—Distribution of protactinium-231 between TBP and nitric acid.
○ forward D_{Pa}
△ *strip* D_{Pa}

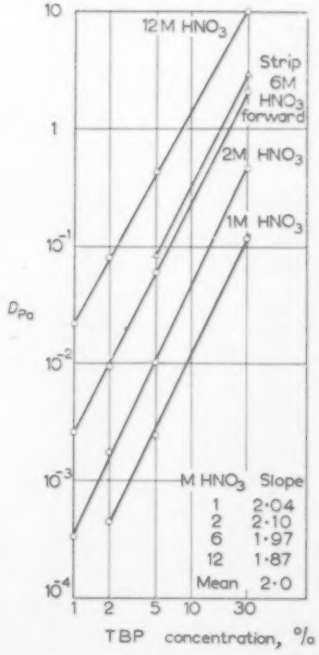

FIG. 3.—Variation of D_{Pa} with TBP concentration.
○ forward D_{Pa}
△ *strip* D_{Pa}

Variation of D_{Pa} with total nitrate concentration and with hydrogen-ion concentration in HNO_3–sodium nitrate mixtures

The *strip* D_{Pa} increases approximately with the square of the total nitrate concentration (Table 1); however, the solutions were not maintained at constant ionic strength. Comparative figures for thorium are taken from the work of HESFORD *et al.*[9]

D_{Pa} is approximately independent of H^+ concentration in HNO_3–$NaNO_3$ mixtures at total nitrate concentrations of 2 M and 4 M (Table 1) but D_{Pa} shows a

TABLE 1.—VARIATION OF D_{Pa} WITH NITRATE AND HYDROGEN-ION CONCENTRATION

Total nitrate concentration, M	Hydrogen-ion concentration, M (calculated from degree of dissociation)	D_{Pa}	D_{Th} (19% TBP)
2	1	0·45	1·13
	2	0·52	
4	1	1·95	9·2
	4	2·2	
6	1	5·0	33
	3	3·0	
	5	5·2	

complex dependence at a total nitrate concentration of 6 M (see similar effect on cation exchange resin, Part II).

Conclusions

Apart from the presence of a small amount of inextractable (polymer) material, the behaviour of 10^{-5} M protactinium in nitric acid has the characteristics of many other metal nitrates towards TBP. These other cases have been satisfactorily interpreted[10] as the selective extraction by TBP of uncharged nitrato complexes from the mixtures of cationic, non-ionic and anionic nitrato complexes e.g., for M^{3+}:

$$MNO_3^{2+} \rightleftharpoons M(NO_3)_2^{+} \rightleftharpoons M(NO_3)_3 \rightleftharpoons M(NO_3)_4^{-} \text{ etc.}$$
$$\downarrow$$
$$\text{extracted by TBP}$$

For protactinium(V), other evidence points to partial hydrolysis of the Pa^{5+} in nitric acid. If, for example, this has proceeded to $Pa(OH)_2^{3+}$ or PaO^{3+} one can postulate the following series of nitrato complexes (in rapid equilibrium with one another):

$$[Pa(OH)_2NO_3]^{2+} \rightleftharpoons [Pa(OH)_2(NO_3)_2]^{+} \rightleftharpoons Pa(OH)_2(NO_3)_3 \rightleftharpoons [Pa(OH)_2(NO_3)_4]^{-}$$
$$\downarrow$$
$$\text{extracted by TBP}$$

[9] E. HESFORD, H. A. C. MCKAY and D. SCARGILL, *J. Inorg. Nucl. Chem.* **4**, 321 (1957).
[10] J. M. FLETCHER, *Progress in Nuclear Energy* Series 3, Vol. I, p. 105, Pergamon Press, London (1956).

The Effect of Fluoride on Nitrate Solutions of Protactinium and Thorium

The influence of fluoride ions on the extraction of protactinium is of particular interest in chemical processing since it is usual to add fluoride in order to dissolve irradiated thorium and thoria. We have therefore examined separately the influence of traces of fluoride on the extraction by TBP both of thorium and of protactinium: the presence of aluminium nitrate which is often used to nullify the presence of fluoride ions, has also been included.

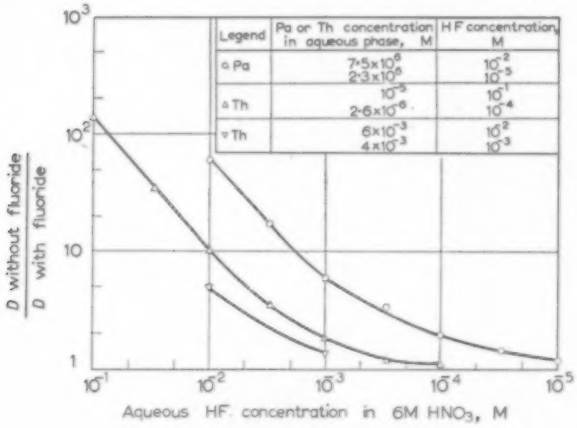

FIG. 4.—The effect of HF on D_{Pa} and D_{Th}.

The addition of hydrogen fluoride to nitric acid solutions of protactinium and of thorium reduced D_{Pa} and D_{Th} owing to the formation of inextractable or very slightly extractable fluoro-complexes.

Results

Previous work[11] on fluoro-complexing of thorium in nitric acid solution has been limited to conditions of process interest. Fig. 4 shows the influence of fluoride on the distribution of thorium at totals of 10^{-2} and 10^{-5} M Th between 6 M HNO_3 and 30 per cent TBP. These measurements were made with the thorium initially in the organic phase and the values of the *strip* D_{Th} were the same for stirring times of 2½ and 60 min.

Fig. 5 gives the percentage of the thorium in the aqueous phase which is complexed by fluoride at HF concentrations from 10^{-1} to 10^{-4} M, deduced from the results given in Fig. 4 on the assumption that the fluoro-complexes are negligibly extracted.

The influence of fluoride on the extraction of protactinium under similar conditions is included in Fig. 4 and Fig. 5. Stirring times of 2½ and 60 min gave the same results for *strip* D_{Pa}: this indicates rapid attainment of equilibrium between the fluoro- and nitrato-complexes.

The results of MARTIN plots (Fig. 1) on protactinium solutions in 6 M HNO_3 containing varying amounts of fluoride show that the amount of inextractable

[11] H. A. C. MCKAY and J. M. FLETCHER, *Progress in Nuclear Energy* Series 3, Vol. I, p. 158. Pergamon Press, London (1956).

"polymeric" protactinium (not in rapid equilibrium with the fluoro- or nitrato-complexes) remains constant at a given protactinium concentration, e.g. 10^{-5} M. The nature of these plots also establishes that the fluoro-, like the nitrato-complexes are liable but are negligibly extracted by 30 per cent TBP in this system.

Derivation of formation constants

Apart from the practical interest of the above results, information can be derived from them on the formation constants for certain fluoro-complexes.

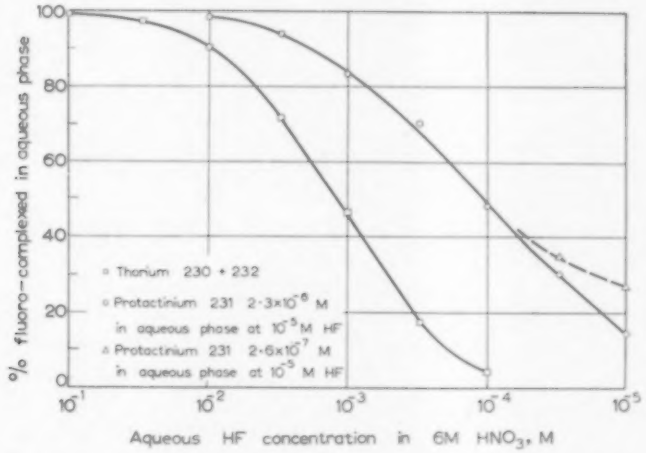

FIG. 5.—Fluoro-complexing of protactinium and thorium in nitric acid solution.

For fluoro-complexing of cations of the type:

$$M^n + HF \rightleftharpoons MF^{n-1} + H^+,$$

$$M^n + 2HF \rightleftharpoons MF_2{}^{n-2} + 2H^+$$

the formation constants are given by

$$K_1 = \frac{[MF^{n-1}][H^+]}{[M^n][HF]} \qquad \text{and} \qquad K_2 = \frac{[MF_2{}^{n-2}][H^+]^2}{[M^n][HF]^2},$$

where $[M^n]$ is the total concentration of M not fluoro-complexed, and activity coefficients are assumed constant. If

$$X = \frac{\text{distribution coefficient without fluoride}}{\text{distribution coefficient with fluoride}}$$

we have[12] $X = 1 + K_1[HF] + K_2[HF]^2 + \ldots$, hence a plot of $(X - 1)/[HF]$ vs. [HF] should give a straight line of slope K_2 and intercept K_1 at $[HF] = 0$. Slight curvature would be introduced if the [HF] was sufficiently high for the third complex to be present in appreciable amount.

For thorium, the plot of $(X - 1)/[HF]$ vs. [HF] shows considerable scatter over the range 10^{-4} to 10^{-4} M HF and the values of K_1 and K_2 can only be given approximately as 1000 ± 200 and 4000–7000 respectively. A knowledge of the

[12] H. A. C. McKAY, *AERE/C/R*-884 (1952).

nitrato-complexing constants for thorium allows the equilibrium constant for the equation:

$$Th^{4+} + HF \rightleftharpoons ThF^{3+} + H^{+}(K_1')$$

to be calculated, since the thorium not fluoro-complexed will be predominantly nitrato-complexed as well as aquo-complexed. Values in the literature[13,14] indicate that 98 per cent of the thorium is nitrato-complexed in 6 M HNO_3 i.e., only 1/50 of the thorium exists as Th^{4+}. For thorium therefore, K_1 must be increased by a factor of 50 to give $K_1' \simeq 5 \times 10^4$. This can be compared with the value of $4{\cdot}5 - 5 \times 10^4$ deduced for the first fluoro-complex[14,15] in perchloric acid–sodium perchlorate mixtures up to an ionic strength of 6. The exact agreement must be regarded as fortuitous since activities in the perchlorate system could well be different from those in 6 M HNO_3.

For protactinium, the plot of $(X - 1)/[HF]$ vs. [HF] appears to be anomalous at concentrations less than 10^{-3} M of HF, since a negative slope is given at 10^{-3} M HF, and a normal positive slope at concentrations of HF greater than 10^{-3} M. The shape of the usual sigmoid curve of Fig. 5 flattens off at low HF concentrations with low protactinium concentrations. This is very probably due to traces of fluoride present in the HNO_3 and H_2O, especially when HF concentrations of the order of 10^{-5} to 10^{-6} M are studied. It has therefore not been possible to calculate K_1 for protactinium, but from the concentration of HF required to complex 50 per cent of the thorium or protactinium it is seen that fluoro-complexing of protactinium in 6 M HNO_3 is of the order of ten times stronger than that of thorium.

The effect of $Al(NO_3)_3$ *on* D_{Pa} *between* 30 *per cent* TBP *and* HNO_3–HF *mixtures*

The addition of an excess of an aluminium salt to a HNO_3–HF solution containing protactinium reduces the extent of fluoro-complexing of the protactinium and allows it to be extracted by a solvent. A quantitative study is given in Fig. 6 of the effect of the aluminium nitrate concentration on D_{Pa} into 30 per cent TBP from 2 M HNO_3 containing 10^{-1} to 10^{-2} M HF at a constant total concentration of 10^{-5} M protactinium-231. Comparative figures for approximately 10^{-5} M thorium-230 are included for 0·5 M aluminium. Fig. 7 gives the percentage of fluoro-complexed protactinium in the aqueous phase assuming that the difference between D_{Pa} with both HF and aluminium present and D_{Pa} with only aluminium present is due to the presence of inextractable fluoro-complexes of protactinium.

The addition of a stoicheiometric amount of aluminium (1Al : 3HF) reduces the percentage of fluoro-complexed protactinium from >96 per cent to 85 per cent in each case. Comparison of the figures for thorium and protactinium at 0·5 M $Al(NO_3)_3$ indicates that the addition of aluminium reduces the fluoro-complexing of thorium to a greater extent than the fluoro-complexing of protactinium.

Solvent Extraction of Protactinium by Butex

Extraction and strip values of D_{Pa} are given in Table 2 for 10^{-5} M protactinium in 2–8 M HNO_3 with butex presaturated with the appropriate concentration of acid.

[13] R. A. DAY and R. W. STOUGHTON, *J. Amer. Chem. Soc.* **72**, 5662 (1950).
[14] E. L. ZEBROSKI, H. W. ALTER and F. K. HEUMANN, *J. Amer. Chem. Soc.* **73**, 5646 (1951).
[15] H. W. DODGEN and G. K. ROLLEFSON, *J. Amer. Chem. Soc.* **71**, 2600 (1949).

A discussion of these data in relation to the extractability of other elements is given later.

Extraction of Protactinium by Dialkylphosphoric Acids

Extraction by these acids has been studied both on account of the formation of dibutylphosphate (DBP) by hydrolysis or radiolysis in TBP systems and also to provide information on the nature of the protactinium species in nitric acid solutions.

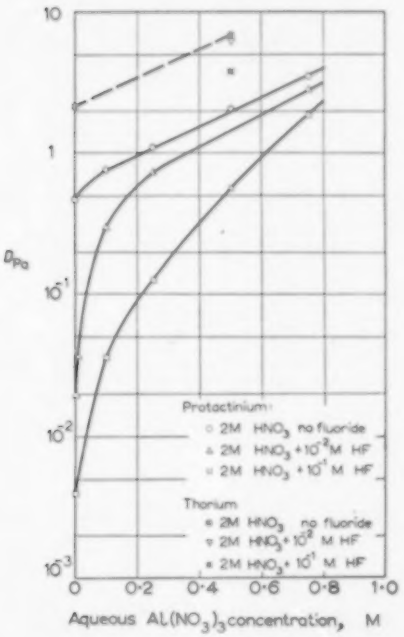

FIG. 6.—The effect of HF and $Al(NO_3)_3$ on the distribution of protactinium between 30% TBP and nitric acid.

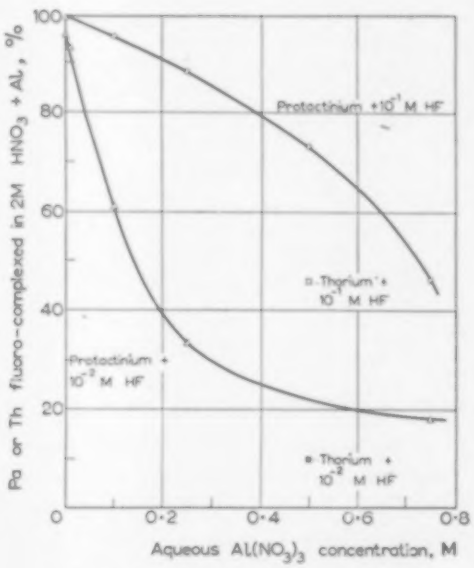

FIG. 7.—Fluoro-complexing of protactinium and thorium in nitric acid–aluminium nitrate solution.

TABLE 2.—EXTRACTION OF PROTACTINIUM BY BUTEX

HNO_3 (M)	2	3	4	5	6	8
Extraction D_{Pa}	0·02	0·25	0·61	1·20	1·60	2·10
Strip D_{Pa}	—	0·25	0·67	1·25	1·80	2·30

Variation of D_{Pa} with DBP *concentration in* TBP

Values of D_{Pa} given in Table 3 were obtained by extraction of a 10^{-5} M solution of protactinium in 6 M HNO_3 with 30 per cent TBP containing DBP. All extractions were with equal-volume phases and the aqueous solution contained 2 per cent of the protactinium in a TBP-inextractable form. Contamination of TBP by traces of DBP of the order of 10^{-4} M has been detected by the curvature which it introduces into MARTIN plots (cf. Fig. 1).

Failure of DBP *to extract polymerized forms of protactinium*

Extraction of protactinium by solutions of DBP in organic solvents is limited to those species which are not polymerized. The analytical method of FUDGE and WOODHEAD[16] for the extraction of protactinium by 0·07 M DBP in dibutylether probably depends on the existence of the element entirely as nitrato or oxalato complexes. We find that in the absence of oxalate the same solvent does not remove any TBP-inextractable protactinium that may be present (~12 per cent in a particular solution) even after successive extractions.

TABLE 3.—VARIATION OF D_{Pa} WITH DBP CONCENTRATION

Concentration of DBP in 30% TBP (M)	D_{Pa} (for 6 M HNO_3)
0	2·6
10^{-4}	3·0
5×10^{-4}	3·8
10^{-2}	50

Extraction by dialkylphosphoric acids

To obtain information on metallic species by distribution measurements with dialkylphosphates (cf. uranyl from nitrate,[17,18] sulphate,[19,20] and phosphate[21] solutions), measurements over a range of dialkylphosphate concentration are desirable. With DBP concentrations $<10^{-2}$ M in kerosene and dibutylether diluents irreproducible results have been obtained, possibly due to the very low solubility of the protactinium-DBP complex. Slightly better results were obtained with benzene or toluene as diluent, which is in agreement with the higher solubility of DBP complexes in these diluents (cf. uranium[18]).

With the higher dialkylphosphate, di(2-ethylhexyl) phosphate, HDEHP, results were reproducible and therefore distribution coefficients have been measured using solutions of this acid in odourless kerosene. To avoid complications due to polymeric forms of protactinium, strip rather than forward values of D_{Pa} were measured. The reaction rate was such that a stirring time of at least 5 min was necessary to achieve equilibrium (*strip* D_{Pa} into 2 M HNO_3 from 10^{-4} M HDEHP was 42, 5·5 and 5·3 for 2, 5, and 15 min stirring respectively).

Values of *strip* D_{Pa} as a function of HDEHP concentration for 10 min equilibration with an equal volume of 2 M HNO_3 and of 10 M HNO_3 were:

HDEHP Concentration, (M)	10^{-4}	5×10^{-4}	10^{-3}	5×10^{-3}
D_{Pa}, 2 M HNO_3	5·2	25	50	270
D_{Pa}, 10 M HNO_3	2·6, 3·6	48	215	>2000

[16] A. J. FUDGE and J. WOODHEAD, *Chem. & Ind.* 1122, (1957).
[17] E. K. HYDE, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1955. Vol. 7, p. 290. United Nations (1956).
[18] J. KENNEDY, *AERE*, Unpublished results.
[19] C. A. BLAKE, K. B. BROWN and C. F. COLEMEN, *ORNL* 1903 (1955).
[20] D. I. O. JOHNSON and G. L. MILWARD, *CRL/AE*-143 (1956).
[21] B. J. THAMER, *J. Amer. Chem. Soc.* **79**, 4298 (1957).

Log-log plots of D_{Pa} against HDEHP concentration give slopes of 1·0 at 2 M HNO_3 and ~2 at 10 M HNO_3.

Discussion

The above results with HDEHP support the hypothesis of KENNEDY[18] that two mechanisms operate in the extraction of metals by dialkylphosphoric acids. For a general cation, M^{n+}, we have

(i) $$M_{aq}^{n+} + n\text{HDEHP}_{org} \rightleftharpoons M(\text{DEHP})_{n,org} + nH_{aq}^{+} \quad \text{and}$$

(ii) $$M_{aq}^{n+} + nNO_3^-{}_{aq} + m\text{HDEHP}_{org} \rightleftharpoons M(NO_3)_n\cdot(\text{HDEHP})_{m,org}$$

For (i) $$K_e = \frac{[M(\text{DEHP})_n][H^+]^n}{[M^{n+}][\text{HDEHP}]^n} \quad \text{and} \quad D_M = K_e \cdot \frac{[\text{HDEHP}]^n}{[H^+]^n}, \quad \text{and for}$$

(ii) $$K_e' = \frac{[M(NO_3)_n(\text{HDEHP})_m]}{[M^{n+}][NO_3]^n[\text{HDEHP}]^m} \quad \text{and} \quad D_M = K_e' \cdot [\text{HDEHP}]^m \cdot [NO_3]^n$$

without consideration of activity coefficients.

TABLE 4.—VARIATION OF D_{Pa} WITH $[HNO_3]$ FOR EXTRACTION BY TOA IN BENZENE (EQUAL VOLUME PHASES, STIRRED 2 MIN AT 20°C)

Conc. of TOA (M)	HNO_3 1	2	4	6	8	12 M
0·1	0·058	0·083	0·14	0·20	0·12	0·079
0·5	0·087	0·33	0·97	1·34	—	0·60

At 2 M HNO_3, protactinium may be extracted as a singly charged cation ($D_{Pa} \propto [\text{HDEHP}]$) but this is not certain, since D_{Pa} should be inversely proportional to the $[H^+]$ and experimentally D_{Pa} was approximately independent of $[H^+]$ from 0·5 to 2·0 M H^+ at 2·0 M total nitrate concentration in $LiNO_3$–HNO_3 mixtures. A study of H^+-dependence at lower $[H^+]$ is not possible due to hydrolysis of the protactinium. At 10 M HNO_3 the dependence of D_{Pa} on $[\text{HDEHP}]^2$ is probably due to the second mechanism, and is analogous to TBP complexing (cf. 2 TBP per protactinium).

The Extraction of Protactinium with Tri-Octylamine

Tri-*n*-octylamine (TOA) in contact with HNO_3 forms ions of the structure $(n\text{-octyl})_3\,NH^+\cdot NO_3^-$ of which the NO_3^- can exchange with other anions in a manner analogous to a solid ion-exchange resin.[22] The variation of D_{Pa} with HNO_3 concentration for extraction by solutions of TOA in benzene is shown in Table 4. No significant difference was found for stirring times of 2 and 90 min using TOA without diluent.

The variation of D_{Pa} with HNO_3 concentration is similar to the variation of the uptake of protactinium by the anion-resin DeAcidite FF with the HNO_3 concentration up to 6 M (see Part II).

[22] K. B. BROWN, C. F. COLEMAN, D. J. CROUSE, J. O. DENIS and J. G. MOORE, A.E.C.D. 4142 (1954).

For an exchange reaction of the type:

$$M(NO_3)_x^{n-} + nRH{\cdot}NO_3 \rightleftharpoons RH_n{\cdot}M(NO_3)_x + nNO_3^-,$$

the distribution coefficient, D_M, is proportional to the n'th power of C_R, the concentration of $RH \cdot NO_3$ in the organic phase. The proportionality constant, K, is given by

$$K = \frac{K_1 \cdot f_x \cdot \gamma'_{M(NO_3)_x^{n-}} \cdot \gamma'^{n}_{RHNO_3}}{C_S{}^n \cdot \gamma'^{n}_{NO_3^-}}$$

where K_1 is the equilibrium constant for the exchange reaction,

f_x is the fraction of M in solution as $M(NO_3)_x^{n-}$,

C_S is the nitrate ion concentration in solution, and

γ_x is the activity coefficient of x, and is assumed to be constant.

The slope of the log-log plot of D_M vs. C_R at constant C_S gives the charge on the M-anion assuming that C_R and $[M(NO_3)_x^{n-}]$ are small but that $C_R \gg [M(NO_3)_x^{n-}]$ The results for extraction from 6 M HNO_3 as a function of [TOA] are:

TOA	0·02	0·05	0·10	0·50	2·34 M
D_{Pa}	0·05	0·10	0·20	1·34	8·6

The slope of the log-log plot is unity which indicates a charge of -1 on the protactinium anion. Other results in 2–12 M HNO_3 agree with this charge.

Comparison of the Solvent Extraction of Protactinium with that of other Elements in HNO_3 *Solution*

Protactinium occupies an intermediate position compared to other elements in respect to TBP extraction from HNO_3 solution. For example at an aqueous acidity of 2 M, the order of distribution coefficients with 20 per cent TBP is:[10]

$$U(VI) > Np(VI) > Pu(IV) > Pu(VI) > Th(IV) > Np(IV) > Pa(V) > Zr(IV) > \text{trivalent metals}$$

The curve which relates D_{Pa} to the aqueous acidity increases continuously with acidity, as for Zr(IV)[23] and Nb(V),[24] whereas the curves for Th(IV), Pu(IV), and U(VI) etc. pass through a maximum at moderate acidities: the curves for Th(IV) and Pa(V) cross (Fig. 8). The relative distribution coefficients of U(VI), Th(IV) and Pa(V) are:

Acid concn. (M)	TBP concn. (%)	D_U	D_{Th}	D_{Pa}
6	30	>100	6	3
2	5	2	0·075	0·019

U(VI) can therefore be easily separated from Th(IV) and Pa(V) by solvent extraction with TBP over a wide range of conditions.

Protactinium also occupies an intermediate position compared to other elements[25] for extraction into butex from nitric acid solution. At an aqueous acidity of 3 M the order of extraction is:

[23] K. ALCOCK, F. C. BEDFORD, W. H. HARDWICK and H. A. C. MCKAY, *J. Inorg. Nucl. Chem.* **4**, 100 (1957).
[24] C. J. HARDY and D. SCARGILL, Unpublished work.
[25] G. F. BEST, E. HESFORD and H. A. C. MCKAY, *Proc. Paris Conf., I.U.P.A.C.* (1957).

Pu(IV) > Np(VI), Pu(VI), U(VI) > Np(IV) > Pa(V) > Th(IV) > trivalent metals.

The fluoro-complexing of protactinium in HNO_3 is of the order of ten times stronger than that of thorium under similar conditions. This allows protactinium to be placed in the following series with respect to fluoro-complexing:[12]

$$H^+ < Fe^{3+} < UO_2^{2+} < Al^{3+} < Th^{4+} < Pa(V) \simeq Zr(IV)$$

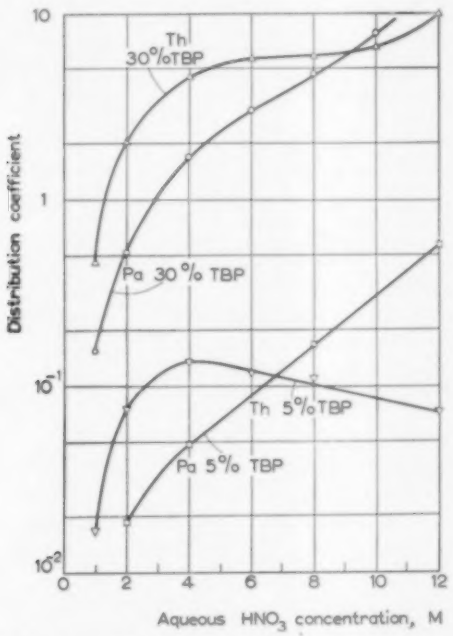

FIG. 8.—Comparison of the TBP extraction of protactinium(V) and thorium(IV).

PART II—ION EXCHANGE OF PROTACTINIUM, THORIUM AND URANIUM AND THE ADSORPTION OF PROTACTINIUM ON SOLIDS

Little detailed work has been published on the adsorption of protactinium, thorium and uranium on ion-exchange resins from HNO_3 solution. The adsorption of protactinium has been studied in greater detail from HCl–HF solutions[26,27] than from HNO_3 solutions. SULLIVAN and STUDIER[28] found that thorium and protactinium can be completely adsorbed from 0·1–2 M HNO_3 on a cation-exchange resin. CARSWELL[29] has reported distribution coefficients for thorium and uranium on DeAcidite FF anion-resin from 2–8 M HNO_3. In order to extend our knowledge of the adsorption of these elements from HNO_3 solution, we have studied the adsorption of protactinium on DeAcidite FF resin and on active solids, and of protactinium, thorium and uranium on ZeoKarb 225 cation-resin.

[26] K. A. KRAUS, G. E. MOORE and F. NELSON, *J. Amer. Chem. Soc.* **78**, 2692 (1956).
[27] A. G. MADDOCK and W. PUGH, *J. Inorg. Nucl. Chem.* **2**, 114 (1956).
[28] SULLIVAN and STUDIER, quoted by ELSON[1] p. 110.
[29] D. J. CARSWELL, *J. Inorg. Nucl. Chem.* **3**, 384 (1957).

Experimental

Cation and anion exchange resins were converted from the sodium and chloride forms respectively to the hydrogen and nitrate forms by repeated treatment with ammonium hydroxide and then nitric acid. They were stored under dilute HNO_3 and a measured volume (of the order of 1 ml) of wet resin was conditioned with the required concentration of HNO_3 before use. Distribution coefficients with resins were determined in glass centrifuge tubes (fitted with glass stirrers) except where otherwise stated. Negligible deposition of protactinium on the walls was found when solutions in 1–10 M HNO_3 were stirred for 1–24 hr in glass tubes. The protactinium-231 stock solution was one of those referred to in Part I with a protactinium α-purity >99·5 per cent. Uranium-233 tracer was available in dilute HNO_3 solution; α-pulse analysis indicated an α-purity of 99·8 per cent. The thorium was available as a mixture of 12 per cent thorium-230/88 per cent thorium-232 at a total thorium concentration of 4 mg/ml of dilute HNO_3, with small amounts of inactive scandium and calcium impurities.[20]

The distribution coefficient, D_V, is calculated from α-activity per ml of resin/α-activity per ml of solution at equilibrium. The α-activity adsorbed was obtained by difference between the initial and final activity in solution.

Rate of Exchange on Ion-exchange Resins

The rate of adsorption of protactinium on a number of 1 ml samples of 300 mesh (<50 μ diameter) H^+-form ZeoKarb 225, and <50 μ diameter NO_3^--form DeAcidite FF from 10^{-5} M protactinium in 6 M HNO_3 at 20°C are given in Fig. 9. Equilibrium is reached after stirring for <15 min on ZeoKarb 225, and for 1–2 hr on DeAcidite FF. Distributions were therefore measured after 1 hr equilibration on ZeoKarb 225 and 3 hr on DeAcidite FF and periodically checked after 24 hr to confirm that equilibrium had been reached.

The percentage of protactinium adsorbed on −16 + 50 mesh ZeoKarb 225 from 10^{-5} M solution in 0·5–4 M HNO_3 was identical for equilibration times of 1, 3, and 24 hr, hence equilibrium under these conditions is also reached in <1 hr.

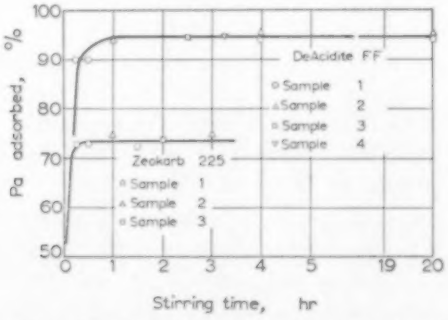

FIG. 9.—Adsorption of protactinium on resins as function of stirring time.

The Variation of D_V with HNO_3 Concentration

The adsorption of protactinium, thorium, and uranium from approximately 10^{-5} M solutions in HNO_3 at 20°C is given in Figs. 10 and 11 for DeAcidite FF and ZeoKarb 225 respectively.

For protactinium on ZeoKarb 225 good agreement was obtained between "forward" distributions with barren resin and "strip" distributions from the loaded resin.

[20] D. J. CARSWELL, D. W. CLELLAND and J. M. FLETCHER, *J. Inorg. Nucl. Chem.* **3**, 147 (1957).

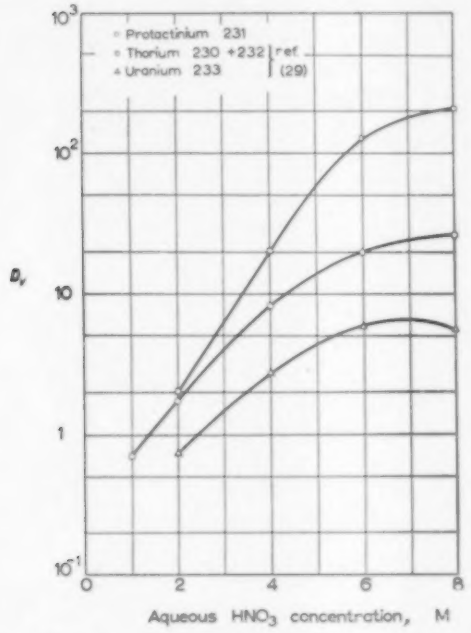

FIG. 10.—Adsorption of thorium(IV), protactinium(V), and uranium(VI), on DeAcidite FF resin.

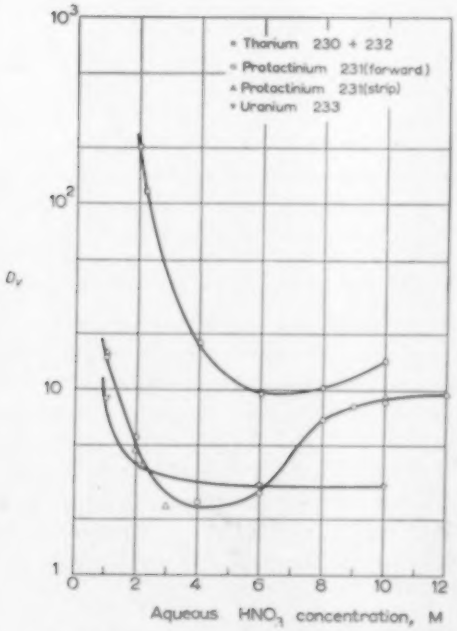

FIG. 11.—Adsorption of thorium(IV), protactinium(V), and uranium(VI), on ZeoKarb 225 resin.

The ZeoKarb 225 resin was stable to prolonged contact with 12 M HNO_3 but the 300 mesh DeAcidite FF rapidly deteriorated in >8 M HNO_3 to give finer material which could only be slowly centrifuged.

A log-log plot of D_V against HNO_3 concentration is given in Fig. 12 for protactinium on ZeoKarb 225 resin. The slope of 1·6 indicates the approximate charge

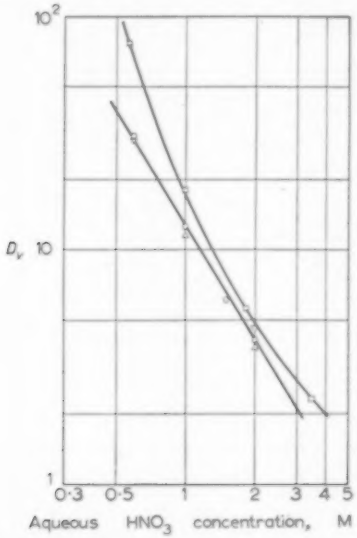

FIG. 12.—Determination of the charge on the protactinium cation.
○, forward D_V, −300 mesh resin in glass.
▽, strip D_V, −300 mesh resin in glass.
△, forward D_V, −16 + 50 mesh resin in glass.
□, forward D_V, −16 + 50 mesh resin in polythene

on the cationic species of protactinium on the resin (cf. the method of STRICKLAND[31]). Good agreement was obtained in glass tubes between D_V on finer than 300 mesh and on −16 + 50 mesh ZeoKarb 225 resin. However, data on −16 + 50 mesh resin in polythene tubes are slightly different from those in glass.

Ion-exchange of Protactinium from HF–HNO_3 *Solution*

From a 10^{-5} M Pa solution in 10^{-2} M HF–6 M HNO_3, 16 per cent of the protactinium was adsorbed on ZeoKarb 225 cation resin and 75 per cent on DeAcidite FF anion-resin. With no resin present in the above solution, TBP extraction indicates that ~98·5 per cent of the protactinium is fluoro-complexed and inextractable.

The Adsorption of Protactinium on Solids

The removal of traces of protactinium by passing "process solutions" through a column of silica-gel has been reported by GRESKY,[32] but no details have been given. It is well known that nitric acid solutions of protactinium are more likely to show hydrolytic and irreversible behaviour in contact with glass and metal surfaces than

[31] J. D. H. STRICKLAND, *Nature, Lond.* **169**, 620, 738 (1952).
[32] A. T. GRESKY, *Proceedings of International Conference on Peaceful Uses of Atomic Energy, Geneva,* 1955. Vol. 8, p. 540. United Nations (1956).

are HCl and HF solutions. However, the solutions of protactinium-231 used in the present extraction and adsorption experiments were stable towards glass surfaces during the time of the experiments, 2 min to 24 hr, but this does not preclude the possibility of gradual adsorption of protactinium on glass surfaces over much longer periods of contact.

(a) *Silica:* an uptake of 80 per cent of the protactinium after 1 min and 85 per cent after 30 min was obtained on 0·025 g of precipitated silica per ml of 10^{-5} M Pa in 6 M HNO_3.

(b) *Cellulose:* adsorption of 20 per cent of the protactinium was obtained on 0·1 g Whatman No. 1 per ml of 10^{-5} M Pa in 6 M HNO_3 after stirring for both 15 and 30 min. This accounts for the strong adsorption of trace protactinium from nitric acid solution by the filter-paper used in paper-chromatography.

(c) *Graphite*: adsorption of protactinium-231 from 6 M HNO_3 by finely divided nuclear grade graphite (68·5 m^2/g) in polythene at 20°C varied linearly from 2 μg Pa/g of graphite at 0·22 μg Pa/ml of solution to 20 μg Pa/g of graphite at 2·34 μg Pa/ml and gave a mean distribution coefficient

$$\frac{\mu\text{g Pa adsorbed/g graphite}}{\mu\text{g Pa/ml solution}} = 9{\cdot}0 \pm 0{\cdot}5$$

Identical results were obtained for equilibrations for 1 hr and 3 hr. The distribution coefficient was approximately constant for ratios of volume of liquid/weight of graphite from 5 to 40. At 20 μg Pa/g graphite in equilibrium with $\sim 10^{-5}$ M Pa in 6 M HNO_3 each atom of protactinium occupies an area of graphite surface of $\sim 1{\cdot}3 \times 10^{-11}$ cm^2 (or a square of side 360 Å). A higher concentration of protactinium will therefore be necessary before the graphite surface is saturated.

Discussion and Comparison of the Ion Exchange of Protactinium with that of other Elements in HNO_3 *Solution*

The fact that protactinium(V) can form cationic and anionic species in HNO_3 solution is demonstrated by the adsorption on both cation and anion-exchange resins, as is also found with uranium and thorium in nitric acid solution. The distribution coefficient for protactinium on an anion-resin increases as the HNO_3 concentration increases up to 8 M and is compared with those for thorium and uranium in Fig. 10. The following order of adsorption from >4 M HNO_3 solution is found[33] on strong-base anion resins, e.g. DeAcidite FF, Amberlite IRA 400, Dowex 1:

$$\text{Np(IV), Pu(IV)} > \text{Th(IV)} > \text{Pa(V)} > \text{U(VI), Np(VI), Np(V)}$$

The distribution coefficient for protactinium on the cation resin ZeoKarb 225 passes through a pronounced minimum in the region 3–6 M HNO_3, and the extent of adsorption from 1–6 M HNO_3 is very similar to that for UO_2^{2+} (Fig. 11). Although adsorption by cation exchange resins from solutions of high acidity is often anomalous,[34] the enhanced adsorption of protactinium(V) above 5 M nitric acid is significantly different from that of thorium(IV) and uranium(VI) under identical conditions. The effect may be due to conversion of hydroxyl groups by protons to aquo groups, which would increase the average positive charge, and hence the

[33] C. J. HARDY, *Progress in Nuclear Energy* Series 3, Vol. II, Paper 8.2. To be published by Pergamon Press, London (1958).
[34] R. M. DIAMOND, K. STREET and G. T. SEABORG, *J. Amer. Chem. Soc.* **76**, 1461 (1954).

adsorption. Adsorption from 1 M HNO_3 by a strong cation exchanger, e.g. ZeoKarb 225, Amberlite IR 120, is in the order:[33]

$$Th(IV) > Pu(IV) > Pu(III) > U(VI), Np(VI), Np(V), Pa(V)$$

PART III—THE PROBABLE SPECIES OF PROTACTINIUM(V) IN NITRIC ACID SOLUTION

The data in Parts I and II refer to the reproducible behaviour of protactinium towards solvent extraction and ion-exchange from nitric acid solution over the protactinium concentration range from 10^{-4} to 10^{-7} M. Data at $>10^{-4}$ M protactinium are generally not reproducible due to the ease of formation of hydrolysed species especially at a nitric acid concentration less than 3 M. Data at $<10^{-7}$ M protactinium may not be reproducible due to the presence of trace impurities such as fluoride-ion and silica in aqueous reagents, and of DBP in TBP.

The experimental evidence in the reproducible range of conditions indicates the existence of cationic, non-ionic and anionic complexes of protactinium in nitric acid. Interchange between them is fast. This work, like previous work,[35,36] provides no positive evidence for the existence of discreet oxygenated ions such as PaO^{3+}, PaO_2^+. The species of protactinium(V) in nitric acid solutions appear to have little similarity to those of uranium and the succeeding elements which in >1 M HNO_3 can be interpreted in terms of aquo-nitrato complexes of the metal or of oxygenated ions. The results are therefore interpreted in terms of a series of nitrato-hydroxo complexes of formula $[Pa(OH)_n(NO_3)_m]^{5-n-m}$ derived from the hypothetical aquo complex $[Pa(OH)_5(H_2O)_x]$. The value of x is controlled by the (unknown) co-ordination number. The results with TBP indicate that two molecules of TBP are associated with the nitrato complex or complexes extracted from 1–12 M HNO_3. This implies that the probable co-ordination number for protactinium is seven: a typical complex would be $[Pa(OH)_2(NO_3)_3(TBP)_2]$. Our hypothesis relates protactinium(V) in nitric acid to other Group V elements, e.g. to niobium, which exists as hydroxo- rather than as oxo- complexes in hydrochloric acid solutions.[37] Examples of the application of this concept to the results obtained are given below, where for example the behaviour "weakly non-ionic (TBP extraction)" indicates that a small proportion of the protactinium exists as non-ionic species which are extractable by TBP.

	$[HNO_3]$	Behaviour	Suggested species
1.	1–2 M HNO_3	Cationic with resin (average charge, 1·6) and with HDEHP (average charge, 1·0). Weakly non-ionic (TBP extraction)	$[Pa(OH)_3NO_3]^+$ $[Pa(OH)_3(NO_3)_2]$ $[Pa(OH)_2NO_3]^{2+}$ $[Pa(OH)_2(NO_3)_2]^+$
2.	2–6 M HNO_3	Weakly cationic (resins and HDEHP). Moderately non-ionic (TBP) Weakly anionic (resin and TOA).	As in 1, and $[Pa(OH)_2(NO_3)_3]$ $[Pa(OH)_2(NO_3)_4]^-$ $[Pa(OH)(NO_3)_3]^+$ etc.

[35] G. A. WELCH, *Nature, Lond.* **172**, 458 (1953).
[36] K. A. KRAUS, *Proceedings of International Conference on Peaceful Uses of Atomic Energy, Geneva*, 1955. Vol. 7, p. 250. United Nations (1956).
[37] J. H. KANZELMEYER, J. RYAN and H. FREUND, *J. Amer. Chem. Soc.* **78**, 3020 (1956).

3.	6–12 M HNO_3	Strongly non-ionic (TBP) Moderately anionic (average charge, minus 1 from solvent extraction with TOA).	As added in 2.

Aggregates of increasing complexity are formed

(i) at low hydrogen ion concentrations, e.g. on this formulation from cations such as $[Pa(OH)_3]^{2+}$ or $[Pa(OH)_4]^{+}$, or

(ii) in relatively concentrated nitric acid (6–10 M) with Pa $> 10^{-4}$ M, by association from complexes such as $[Pa(OH)_2(NO_3)_3]$.

Acknowledgements—We are indebted to Mr. H. A. C. McKay, Mr. R. P. Bell, F.R.S. and to Dr. K. A. Kraus for helpful discussions, and to Dr. A. G. Maddock and co-workers for the supply of the protactinium-231.

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ACIDIC ESTERS OF ORTHOPHOSPHORIC ACID AS SELECTIVE EXTRACTANTS FOR METALLIC CATIONS—TRACER STUDIES*

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(*Received* 11 *February* 1958)

Abstract—The extraction of Sc(III), Y(III), La(III), Ac(III), Pm(III), Tm(III), and Am(III) into solutions of $(GO)PO(OH)_2$ and $(GO)_2PO(OH)$ in toluene as carrier solvent from aqueous mineral acid phases has been investigated as a function of solvent concentration in the organic phase, hydrogen ion concentration in the aqueous phase, the nature of G, and the position of M(III) in the periodic table, using the radioactive-tracer technique.

The distribution ratio, K, defined for a given radioactive nuclide as its concentration in the organic phase divided by its concentration in the aqueous phase, has been found, for all of the M(III) examples studied, to have an inverse third-power dependency upon the hydrogen ion concentration in the aqueous phase in both the $(GO)PO(OH)_2$ and $(GO)_2PO(OH)$ systems. The solvent dependencies have been found to be direct first-power in the $(GO)PO(OH)_2$ systems and direct third-power in $(GO)_2PO(OH)$ systems.

Since the $(GO)_2PO(OH)$ solvents have been shown to be dimeric, the extracted species is postulated as $M^{III}\{H[(GO)_2PO_2]_2\}_3$. The $(GO)PO(OH)_2$ solvents have been shown to be polymeric. A postulated "dimer" mechanism of extraction suggests that the extracted species is $M^{III}\{H[(GO)PO_2H]_2\}_3$. However, an alternative suggested "infinite polymer" mechanism of extraction seems equally likely.

Specifically, solvents in which G is 2-ethyl hexyl, symbolized as EH, and *para*(1,1,3,3-tetramethyl butyl)phenyl, symbolized as Oϕ, have been investigated. In both the $(GO)PO(OH)_2$ and $(GO)_2PO(OH)$ systems the Oϕ solvent shows a higher K than the EH solvent. In the Oϕ systems, the K_S (an empirical stability constant) for the di-ester is higher than that for the mono-ester for each of the members of the vertical group Sc, Y, La, Ac. In the EH systems, the K_S for the di-ester is the larger for Sc by a factor of approximately 30 and the smaller for Ac by a factor of approximately 10^{-5}.

In all of the systems the K (and K_S) values are compressed toward the bottom of the group in the vertical group, Sc, Y, La, Ac, i.e. the ratio of the K (or K_S) of one element to that of the element immediately below it decreases downward.

THENOYL trifluoroacetone, commonly abbreviated as HTTA, has found wide application in separative extraction of certain metallic cations.[1] This substance, a beta diketone, is considered to ionize in its enol form to produce a univalent anion capable of chelation with a metallic cation to form a six-membered ring. Consequently, in general, the formula of the extracted species is $M(TTA)_b$, where b is the charge on the initial cation; and ideally the distribution ratio, K, is directly dependent upon the bth power of the activity of the HTTA in the organic phase and inversely dependent upon the power of the hydrogen ion activity in the aqueous phase.

The possibility of varying K for a given M^{+b} over a wide range by a suitable combination of HTTA concentration and H^+ concentration has made HTTA an

* Based on work performed under the auspices of the U.S. Atomic Energy Commission.

[1a] J. C. REID and M. CALVIN, *J. Amer. Chem. Soc.* **72**, 2948 (1950); [b] R. E. CONNICK and W. H. MCVEY, *Ibid.* **71**, 3182 (1949); [c] R. A. BOLOMEY and L. WISH, *Ibid.* **72**, 4483 (1950); [d] F. HAGEMANN, *Ibid.* **72**, 768 (1950).

extremely versatile and useful extractant, especially for cations for which it has a strong affinity. However, for the extraction of certain cations for which the affinity is not great, the workable hydrogen ion concentration is so low that severe hydrolysis difficulties are encountered.

By the use of certain other acidic extractants, these extractions may be made in systems sufficiently acidic to avoid hydrolysis although still controlled directly by the solvent concentration and inversely by the acid concentration. The extractants represented by the present study are of the types $(GO)_2PO(OH)$ and $(GO)PO(OH)_2$ where G is an alkyl, aryl or mixed alkyl-aryl group.

PEPPARD *et al.* report the application of di(2-ethyl hexyl) phosphoric acid, an example of the $(GO)_2PO(OH)$ type, to the fractionation of the trivalent lanthanides plus yttrium,[2] to the isolation of carrier-free ^{90}Y, ^{140}La, ^{144}Ce, ^{143}Pr and ^{144}Pr,[3] and to the separation of Bk(IV) from trivalent lanthanides and actinides.[4] SCADDEN and BALLOU[5] report that dibutyl phosphoric acid (containing some of the monobutyl ester) preferentially extracts the "yttrium group" lanthanides from the lower-Z members and also use this solvent in the mutual separation of zirconium and niobium in carrier-free concentration.

PEPPARD and co-workers have described the use of mono(2-ethyl-hexyl) phosphoric acid, an example of the $(GO)PO(OH)_2$ type, in the isolation of Np(IV)[6] and have reported studies of the lanthanide and actinide half-filled shell effects using both mono-esters and di-esters of orthophosphoric acid.[7]

From extensions of the above quoted studies it has become apparent that the respective extraction characteristics of $(GO)_2PO(OH)$ and $(GO)PO(OH)_2$ for a given G differ so widely that many comparative studies of a given array of metallic cations in micro concentrations are invalidated by the presence of a few hundred parts per million of the one ester in the other. Consequently, the present investigation was undertaken for the dual purpose of establishing, for the extraction of a selected group of M(III) cations, the relative effectiveness of "mono" and "di" orthophosphoric esters and the effect of varying G.

EXPERIMENTAL

Sources of materials

All of the phosphoric esters studied were obtained as mixtures of the mono-ester and di-ester containing variable quantities of pyro esters, neutral orthoesters, and free alcohol. Both the octyl mixture, 2-ethyl hexyl isomer, and the *p*-octyl phenyl mixture, *para*(1,1,3,3-tetramethyl butyl) phenyl isomer, were obtained from Victor Chemical Co.

The β-active nuclides 40·2 hr ^{140}La (with parent 12·8 day ^{140}Ba), 2·6 year ^{147}Pm, 58 day ^{91}Y, and 85 day ^{46}Sc were obtained from the Isotopes Division of the Oak Ridge National Laboratory. β-active 129 day ^{170}Tm was prepared by neutron

[2] D. F. PEPPARD, G. W. MASON, J. L. MAIER and W. J. DRISCOLL, *J. Inorg. Nucl. Chem.* **4**, 334 (1957).
[3] D. F. PEPPARD, G. W. MASON and S. W. MOLINE, *J. Inorg. Nucl. Chem.* **5**, 141 (1957).
[4] D. F. PEPPARD, S. W. MOLINE and G. W. MASON, *J. Inorg. Nucl. Chem.* **4**, 344 (1957).
[5] E. M. SCADDEN and N. E. BALLOU, *Analyt. Chem.* **25**, 1602 (1953).
[6] Paper by D. F. PEPPARD, J. L. MAIER, G. W. MASON and S. W. MOLINE, delivered at the *Third Annual Meeting of the American Nuclear Society*, Pittsburgh, Pennsylvania, U.S.A. (1957).
[7] Papers by D. F. PEPPARD, P. R. GRAY, G. W. MASON and W. J. DRISCOLL and by D. F. PEPPARD, G. W. MASON, R. J. SIRONEN and S. MCCARTY, delivered at the *Sixteenth International Congress of Pure and Applied Chemistry*, Paris (1957).

irradiation of highly purified Tm. All of the foregoing tracers were further purified by means of liquid-liquid extraction techniques.*

β-active 6·1 hr ^{228}Ac was isolated, by a liquid-liquid extraction technique,† from a mesothorium source material. α-active 470 year ^{241}Am was obtained from A.N.L. stocks.

Nomenclature

In the interests of brevity and ease of discussion, symbolic formulae, in which H represents a theoretically ionizable hydrogen, are used. For example: HDEHP represents di(2-ethyl hexyl)phosphoric acid, $[(C_2H_5)C_6H_{12}O]_2PO(OH)$, a monobasic acid, and H_2MEHP represents mono(2-ethyl hexyl)phosphoric acid, $[(C_2H_5)C_6H_{12}O]PO(OH)_2$, a dibasic acid. Similarly, HDOϕP and H_2MOϕP represent respectively the di(octyl-phenyl) and mono(octyl-phenyl) esters of orthophosphoric acid, where the octyl-phenyl group is specifically para (1,1,3,3-tetramethyl butyl) phenyl.

In this symbolic system the two type solvents, $(GO)_2PO(OH)$ and $(GO)PO(OH)_2$, are represented respectively as HDGP and H_2MGP, without regard to molecular complexity.

The distribution ratio, K, of a specific nuclide is defined as the concentration of nuclide in the upper divided by the concentration of nuclide in the lower of two equilibrated sensibly-immiscible liquid phases.

The stability constants, K_E and K_S, are defined, and the relationship to K shown, in the Discussion section.

Purification of solvents

The general scheme of separation reported by PEPPARD *et al.*,[2] based on the technique developed by STEWART and CRANDALL,[8] for the mutual separation of HDEHP and H_2MEHP was used, except that benzene and ethylene glycol were used as opposing phases rather than diethyl ether and ethylene glycol. The details of the separations will be reported in a paper dealing with the molecular complexity of these various phosphoric esters.[9]

Determination of distribution ratios

The distribution ratio, K, of a specific nuclide, was determined radiometrically as reported in a previous study.[2] All data were obtained both by "direct" and "reverse" extractions in order to obviate non-equilibrium and hydrolysis difficulties. In the determination of K values in excess of 10^3, extreme care was taken in the clarification of the lower phase, this phase being centrifuged three times, with intermediate transfers to fresh cones, before radiometric assay.

Pre-equilibration in the solvent-dependency and acid-dependency studies was accomplished as follows. Two portions of barren HDGP were contacted successively with two equal-volume portions of barren aqueous acid. The second portion of

* The data of references 2 and 3 were used in devising these separations procedures.

† This procedure, involving removal of divalent radium and lead, trivalent bismuth, an dtetravalent thorium activities, will be reported in detail in a later paper.

[8] D. C. STEWART and H. W. CRANDALL, *J. Amer. Chem. Soc.* **73**, 1377 (1951).

[9] A preliminary study of the molecular complexity of certain HDGP and H_2MGP compounds has been reported by D. F. PEPPARD, J. R. FERRARO and G. W. MASON, *J. Inorg. Nucl. Chem.* **4**, 371 (1957). A detailed report will follow.

solvent phase and the second portion of aqueous phase were then used in the study. In the H_2MGP systems four portions of solvent were contacted successively with one equal-volume portion of aqueous acid, the fourth solvent phase and the aqueous phase being used in the study.

RESULTS AND CONCLUSIONS

Acid dependencies

From Figs. 1, 2, 3 and 4 it is seen that the K for M(III) is inversely third power dependent upon the hydrogen ion concentration in the aqueous phase, the solvents

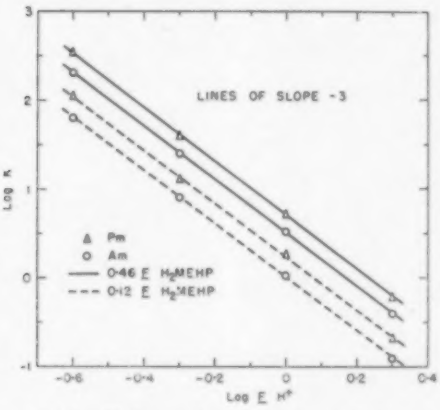

FIG. 1.—Hydrogen ion dependency of the extraction of Am and Pm into H_2MEHP from aqueous HCl + NaCl, 2 F Cl^-.

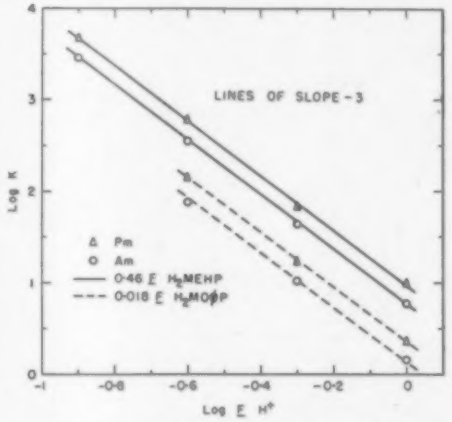

FIG. 2.—Hydrogen ion dependency of the extraction of Am and Pm into H_2MEHP and $H_2MO\phi P$ from aqueous $HClO_4$.

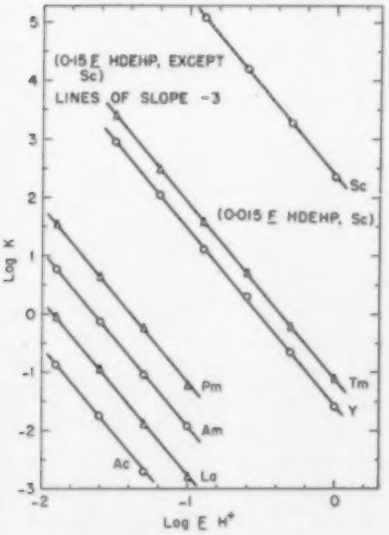

FIG. 3.—Hydrogen ion dependency of the extraction of Ac, La, Am, Pm, Y, Tm, and Sc into HDEHP from aqueous $HClO_4$ + $NaClO_4$, 1 F ClO_4^-.

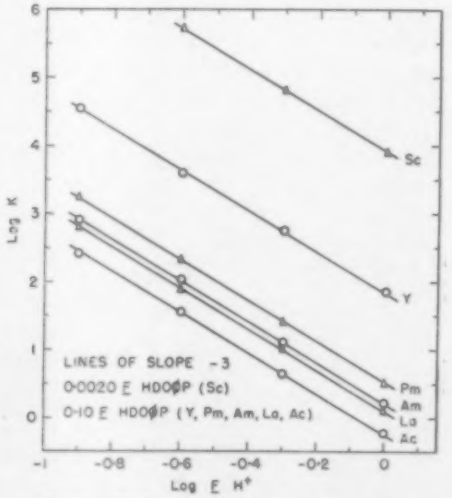

FIG. 4.—Hydrogen ion dependency of the extraction of Ac, La, Am, Pm, Y, and Sc into $HDO\phi P$ from aqueous $HClO_4$ + $NaClO_4$, 1 F ClO_4^-.

being the mono-esters, H_2MEHP and H_2MOϕP, and the di-esters, HDEHP and HDOϕP.

In Fig. 1, this dependence is shown for Am(III) and Pm(III) for two different concentrations of H_2MEHP against an aqueous hydrochloric acid–sodium chloride phase of constant ionic strength. In Fig. 2, the Am(III) and Pm(III) data for the

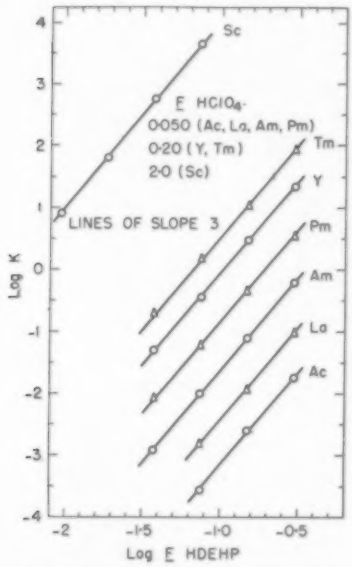

FIG. 5.—Solvent dependency of the extraction of Ac, La, Am, Pm, Y, Tm, and Sc into HDEHP from aqueous $HClO_4$.

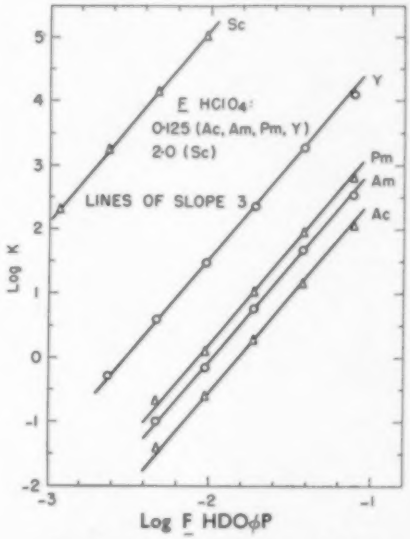

FIG. 6.—Solvent dependency of the extraction of Ac, Am, Pm, Y, and Sc into HDOϕP from aqueous $HClO_4$.

H_2MEHP–$HClO_4$ and H_2MOϕP–$HClO_4$ systems are given. The corresponding data for systems of constant ionic strength, 1·0 F total $HClO_4$ plus $NaClO_4$, are essentially coincident with these data.

In Fig. 3, the inverse third power hydrogen ion dependency is shown for a variety of M(III) cations in the HDEHP–$HClO_4$ system. The corresponding data for the HDOϕP–$HClO_4$ system are given in Fig. 4.

Solvent dependencies

The solvent dependencies for the extraction of M(III) by HDGP are treated first, Figs. 5 and 6, since they appear subject to the simplest interpretation of those studied. In the HDGP (i.e. di-ester) systems the K values are directly third power dependent upon the concentration of HDGP. However, since HDGP has been shown to be dimeric in dry benzene[9] and is assumed to be dimeric in the equilibrated HDGP phases investigated (toluene as carrier solvent) the extracted entity is formulated as $M^{III}[H(DGP)_2]_3$. This formulation is consistent with the observation that gross lanthanide data indicate solvent saturation, for HDEHP, at a 1 : 6 monomer ratio of M(III) to HDEHP, the attempted introduction of additional M(III) into the organic phase resulting in the formation of a gel-like solid.[12]

In the H_2MGP (i.e. mono-ester) systems the solvent dependency data are not so

readily interpreted, due to the existence of the ester as a highly polymeric substance, $(H_2MGP)_x$.[9] The data for Pm(III) and Am(III), Fig. 7, show the solvent dependency to be approximately first power. Assuming the first theory of extraction proposed in the Discussion section and a value of x equal to 6 the theoretical solvent dependency

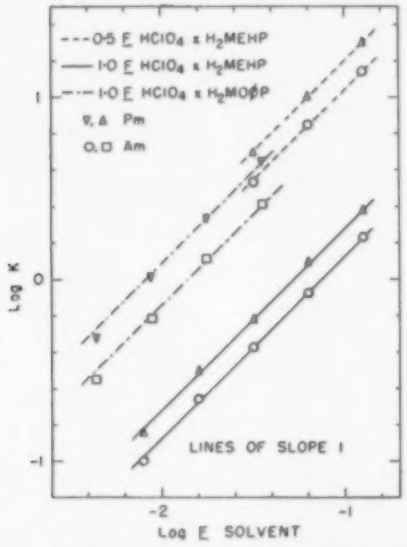

FIG. 7.—Solvent dependency of the extraction of Am and Pm into H_2MEHP and $H_2MO\phi P$ from aqueous $HClO_4$.

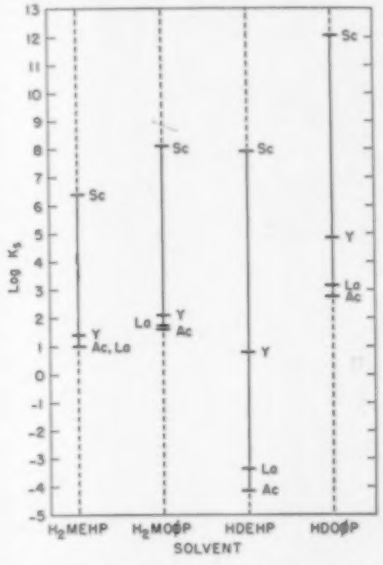

FIG. 8.—Comparison of K_S values for Ac, La, Y, and Sc in H_2MGP–$HClO_4$ and HDGP–$HClO_4$ systems.

is first power. A formulation of the extracted species, consistent with this theory, is $M^{III}[H(HMGP)_2]_3$. This formulation is not to be considered as established.

Selected Z dependencies and "mono, di" effects

Assuming the observed power dependencies for M(III) to be applicable to all of the M(III) cations investigated, the data of the various figures, along with data obtained for this specific purpose, have been translated into K_S values, see Discussion, equations (8) and (9), and plotted in Fig. 8. In the vertical sequence Sc, Y, La, and Ac, it is noted that, as the sequence is descended, the K_S values decrease and the successive K_S values are compressed, i.e. the ratio of K_S for a given element to that for the element immediately below it decreases. It is to be noted that the degree of differentiation between Sc and Y is not greatly affected by a change from a mono-ester to a di-ester but that this change greatly affects the differentiation in the lower part of the sequence.

It is seen that the ratio of K_S(HDGP) to $K_S(H_2MGP)$ is greater than unity for all four of these elements, where G is "Oϕ", and ranges from approximately 30 for Sc to approximately 10^{-5} for Ac, where G is "EH".

G *effects*

From Fig. 8, it is seen that the G effect for H_2MGP is relatively small, the $H_2MO\phi P$ having K_S values approximately five times the corresponding values for H_2MEHP

for Ac, La and Y and approximately 50 times the corresponding value for Sc. The G effect for HDGP is remarkably large, varying from approximately 10^7 for Ac to approximately 10^4 for Sc.

DISCUSSION

Regardless of the state of aggregation of the HDGP extractant, if it exists as a single species in the organic phase and if it ionizes as a monohydric acid and forms a single entity with M^{+b}, then the following analysis may be applied. The equilibrium of interest in the organic phase is represented as:

$$M_O^{+b} + bHY_O \rightleftharpoons MY_{b_O} + bH_O^+.$$

By addition of the pertinent equilibrium expressions representing the distribution of M^{+b} and H^+ between the two phases, organic (O) and aqueous (A), this expression is converted to the following which applies to the two equilibrated phases.

$$M_A^{+b} + bHY_O \rightleftharpoons MY_{b_O} + bH_A^+$$

The corresponding mass law expression, in terms of concentrations rather than activities, to be justified operationally is:

$$[MY_b]_O/[M^{+b}]_A = K_E[HY]_O^b/[H^+]_A^b$$

If M^{+b} is, in the sense of relative concentration, the only M species of importance in the aqueous phase, i.e. the relative concentration of $MY^+_{(b-1)}$ etc. in the aqueous phase is low, the ratio $[MY_b]_O/[M^{+b}]_A$ may be replaced by the distribution ratio, K, to yield:

$$K = K_E[HY]_O^b/[H^+]_A^b \tag{1}$$

This expression is identical to the one long in use in dithizone, HTTA, etc. extraction studies and has been derived more rigorously elsewhere.[10b, 10] However, it is to be noted that in the present discussion HY is a dimer, since the specific examples of HDGP involved in this study have been shown to be dimeric.[9] Consequently, for HDGP the ionization of the extractant and the composite equilibrium may be written, respectively, as:

$$(HDGP)_2 \rightleftharpoons H^+ + H(DGP)_2^-$$

$$M_A^{+b} + b(HDGP)_{2_O} \rightleftharpoons M\{H(DGP)_2\}_{b_O} + bH_A^+ \tag{2}$$

The corresponding version of expression (1) is:

$$K = K_E[(HDGP)_2]_O^b/[H^+]_A^b \tag{3}$$

The solvent dependency and acid dependency data fit expression (3) for all of the M(III) examples studied, regardless of G.

It is assumed that dimeric HDGP, by analogy with dimeric carboxylic acids, such as acetic acid, has the structure presented in Fig. 9. If one of the acidic hydrogen atoms of this dimer is removed by ionization, the resulting singly-charged anion should be capable of chelation with a positively charged metallic ion, on the assumption that the remaining hydrogen bond is not broken. The $M\{H(DGP)_2\}_b$ entity would thus be represented as shown in Fig. 9.

[10] G. H. MORRISON and H. FREISER, *Solvent Extraction in Analytical Chemistry* p. 50. Wiley, New York (1957).

It will be noted, from Fig. 9, that in the postulated structure of the HDGP dimer two phosphorous tetrahedra are joined at two corners by O—H · · · O bridges, so that they are effectually joined edge to edge. Since H_2MGP possesses two acidic H atoms per formula weight, its dimer might logically be expected to contain two phosphorous tetrahedra joined at three corners by O—H · · · O bridges, or effectually

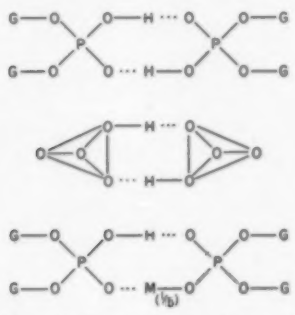

FIG. 9.—Proposed structures of $(GO)_2PO(OH)$ dimer and corresponding complex with M^{+b}.

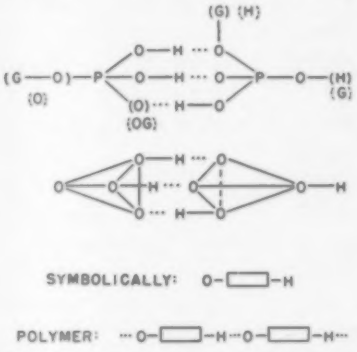

FIG. 10.—Possible structure of postulated dimer and of anhydrous polymer of $(GO)PO(OH)_2$.

joined base to base, as shown in Fig. 10. The theoretical anion, $H(HMGP)_2^-$, resulting from the ionization of one acidic hydrogen from such a dimer should possess even stronger chelating powers than the $H(DGP)_2^-$ anion in the sense that two hydrogen bonds are left intact after chelation so that the P tetrahedra are still joined edge to edge by O—H · · · O bridges. However, a further possibility exists that does not exist for the $H(DGP)_2^-$ entity, namely the stabilization of the $H(HMGP)_2^-$ anion by three O—H · · · O bridges. Such an anion might co-ordinate to a metal ion at a single oxygen or might function by ion-pair association.

On the assumption that in metallic extractions by H_2MGP the extracted species contains mono-ionized dimers, the following composite equilibrium may be postulated:

$$M_A^{+b} + (2b/n)(H_2MGP)_{n_O} \rightleftharpoons M\{H(HMGP)_2\}_{b_O} + bH_A^+ \qquad (4)$$

From expression (4), to be compared with expression (2), K may be related to solvent and acid concentrations as follows:

$$K = K_E[(H_2MGP)_n]_O^{(2b/n)}/[H^+]_A^b \qquad (5)$$

On the assumption that expression (5) is valid, the value of n in a toluene phase equilibrated against an aqueous mineral acid phase may be calculated from the solvent dependency data for M(III) to be approximately 6.

However, the foregoing postulated explanation of extraction by H_2MGP, although attractive from an analogy viewpoint, must be regarded as speculative. It is hoped to establish, by means of optical and molecular weight studies involving gross concentrations of solutes, whether the postulate of extraction by dimers is correct; and it is hoped to extablish a value of n in the equilibrated toluene phase.

This value may differ considerably from that found in dry benzene, since it is found that contacting a toluene solution of H_2MEHP with pure water results in the formation of a gel-like solid. Although this solid may be redissolved by the addition

of mineral acid, its formation in the absence of mineral acid implies a very strong interaction between H_2MGP and H_2O. Consequently, it seems likely that the molecular complexity, and perhaps the type of polymeric structure, in the equilibrated toluene phase should differ from that in dry benzene or naphthalene.

What is perhaps the most attractive alternative explanation of the extraction of M^{+b} by H_2MGP is based on the assumption of "infinite" polymers capable of ionization to produce at least b hydrogen ions per polymeric entity, in the "wet" toluene phase. Although such a polymer is difficult to imagine as composed solely of H_2MGP units, unless the co-ordination number of P is expanded beyond 4, a number of structures for a polymer of this nature containing both H_2MGP and H_2O units may be postulated.

Since in the extraction of M^{+b} by the hypothetical $(HY)_x$ "infinite" polymer the size of M^{+b} may be considered as very small compared with the size of $(HY)_x$, the M^{+b} may be considered as essentially buried in the polymer and held by forces approximating those operative in solid-resin ion exchange. To a first approximation, it may be postulated that in "tracer-level solute" studies only one M^{+b} is held by a given polymeric aggregate, and it is further postulated that only one polymeric aggregate is associated with a given M^{+b}.

The composite equilibrium and the corresponding K expression might then be written as:

$$M_A^{+b} + (HY)_{x_O} \rightleftharpoons M(H_{x-b}Y_x)_O + bH_A^+ \tag{6}$$

$$K = K_E[(HY)_x]_O/[H^+]_A^b \tag{7}$$

The predicted solvent dependency is thus first power, regardless of the value of b in M^{+b}. The observed departures from first power solvent dependency may be explained as due to one or more of the following factors ignored in the foregoing treatment: (1) x may have a series of values rather than a single value, (2) x may, in a given set of experimental conditions, have a discrete value but nevertheless have a different discrete value under a different set of conditions, (3) the assumption that only one M^{+b} is associated with any given polymeric aggregate is not statistically justifiable and the precise effect of this inaccuracy has not yet been evaluated mathematically.

For purposes of inter-comparison of the HDGP and H_2MGP data for M(III) extractions, the respective extractions are represented by the following empirical expressions.

$$K = K_S F_{S_O}{}^3/F_{H_A^+}^3 \tag{8}$$

$$K = K_S F_{S_O}/F_{H_A^+}^3 \tag{9}$$

where F_S represents the formality of the solvent in the organic phase, since the molecular complexity has not been established for H_2MGP under the conditions of the study, F_{H^+} represents the formality of the H^+ ion in the aqueous phase, and K_S is the "extraction constant" which may be related to the K_E of expressions 3, 5, and 7 if the molecular complexity of the solvent is known.

From Fig. 8 it is seen that the order of increasing extractability into HDGP, as measured by K_S, is upward in the periodic system vertical sequence Ac(III), La(III), Y(III), Sc(III). Since the ordinate is a log plot, it follows that equal increments correspond to equal β values, and a larger increment corresponds to a larger β value, where β is the ratio of the K values for two M(III) solutes. It will be noted that the

separability of two adjacent elements in the vertical series, as measured by β, increases upward. As has been reported,[2] Y(III) lies within the lanthanide(III) series, falling between elements 67 and 68 in the HDEHP system.

In this figure, K_S values for both HDGP and H_2MGP are given for the Ac, La, Y, Sc sequence. The "compression effect" of H_2MGP as compared with HDGP is evident.

The comparison of the plots is a striking one, pointing up the fact that tracer-solute data for HDGP may be gravely in error, especially in the lanthanide low-Z range, if contaminant H_2MGP is present. It is, of course, evident that extraction by either HDGP or H_2MGP might be used to effect a rapid separation of Sc(III) from other members of the group.

From Figs. 5–8 the extraction of Am(III) is seen to be greater than that of Ac(III) in both HDGP and H_2MGP systems. Extended studies of actinide(III) and actinide(III)-lanthanide(III) comparative extractions in these systems will be reported elsewhere.

The study is being extended to include: application of these solvent systems to a "group separation" of the actinide(III) group from the lanthanide(III) group, further investigation of mechanism of extraction of M(II) and M(IV) by HDGP, elucidation of the general H_2MGP extraction mechanisms, and investigation of solute hydrolysis by use of the HDGP and H_2MGP solvents. Studies relating to the structure of the HDGP dimers and the H_2MGP polymers will be reported elsewhere.

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J. Inorg. Nucl. Chem., 1958, Vol. 7, pp. 286 to 300. Pergamon Press Ltd., London

LETTERS TO THE EDITORS

A note on the separation of lanthanides from mixtures of their chlorides

(*Received* 3 *February* 1958)

THE dehydration time of hydrated lanthanide chlorides by thionyl chloride lengthens considerably with increase in atomic weight.[1] This trend suggests that there is an increase in the covalent nature of the anhydrous chlorides with increasing atomic weight. Visual examination tends to confirm this since the lower lanthanide chlorides form well defined, hard, needle like crystals whilst the higher chlorides form soft crystals which crumble readily.

A change in the covalent nature of the metal to chlorine bonding would certainly be reflected in the solubilities of the chlorides in organic solvents, and so in the course of the present programme a few simple experiments, described below, have been carried out. These indicate that solubility differences do exist, and that it is possible to effect some separation of the lanthanides by fractional crystallization of their anhydrous chlorides from organic solvents.

Separations were also effected by utilizing the difference in dehydration time of the lanthanide chlorides. Mixtures of lanthanide hydrated chlorides were refluxed with thionyl chloride until one component was completely dehydrated whilst the other was only partially dehydrated. The mixture was then heated strongly in argon to convert the hydrated chloride to oxychloride, and extracted with water to leach out the soluble anhydrous chloride. However, this technique is difficult to control and since it cannot readily be adapted to a multistage separation process it appears to be of less interest than the fractional crystallization method.

Experimental

1. A mixture of 1 g of Nd_2O_3 and 1 g of Dy_2O_3 was dissolved in hydrochloric acid and dehydrated with thionyl chloride. The mixed anhydrous chlorides were then transferred to a stoppered flask and shaken for 5 min with 20 ml of anhydrous acetone. The insoluble matter was filtered off, and the solution was evaporated to dryness. The two components gave the following spectrographic analysis

	Nd	Dy
Soluble fraction (%)	24	76
Insoluble fraction (%)	82	18

A similar experiment was carried out with Dy_2O_3 and Gd_2O_3. In this case the mixture of chlorides was completely dissolved in 200 ml of anhydrous acetone. The solution was then evaporated rapidly until approximately half of the solid had crystallized out and then filtered

	Gd	Dy
Soluble fraction (%)	35	65
Crystalline fraction (%)	59	41

An attempt was made to measure the solubilities of the rare earth anhydrous chlorides in anhydrous acetone but it was found that equilibrium was only slowly attained and that on standing the chlorides reacted with the acetone, and reproducible results could not be attained.

2. A mixture of equal quantities of neodymium and dysprosium oxides were dissolved in hydrochloric acid and dehydrated until about 66 per cent total conversion was obtained. The mixture was then heated strongly in a stream of argon and finally leached out with distilled water.

[1] J. H. FREEMAN and M. L. SMITH, *J. Inorg. Nucl. Chem.* **7**, 224 (1958).

The two fractions gave the following analysis

	Nd	Dy
Soluble fraction (%)	70	30
Insoluble fraction (%)	38	62

A similar experiment with gadolinium and dysprosium oxides gave the following results

	Gd	Dy
Soluble fraction (%)	54	46
Insoluble fraction (%)	32	68

(Spectrographic analysis ±10% accuracy)

Conclusions

The results suggest that fractional crystallization of the anhydrous lanthanide chlorides from acetone would provide a convenient method of lanthanide separation. It is possible that better separations may be obtained by the use of other organic solvents, or by chromatographic techniques.

Acknowledgement—The author is grateful to Mr. F. T. BIRKS for the spectrographic analyses.

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VOL. 7 1958

Thionyl chloride in inorganic chemistry

(*Received* 3 *February* 1958)

ALTHOUGH thionyl chloride is widely used as a chlorinating agent in organic chemistry, it is not generally appreciated that it is a useful reagent in preparative and analytical inorganic chemistry. A number of its reactions have been examined by the authors and are briefly described below.

(1) *Thionyl chloride as a dehydrating agent*

Thionyl chloride reacts readily with water and the dehydration of inorganic chlorides with thionyl chloride is described elsewhere.[1] Anhydrous chlorides are useful starting materials for separation procedures based, for instance, on their volatility or solubility so this simple preparation method makes such procedures much more practicable.

(2) *Reaction of thionyl chloride with sulphates*

Thionyl chloride reacts with sulphuric acid to produce pyrosulphuryl chloride and chlorosulphonic acid;[2] it will also react with sulphates in the presence of a little sulphuric acid. Small quantities of barium, calcium and other insoluble sulphates can be converted to the chlorides by heating them for 2–3 min in a crucible with a small quantity of sulphuric acid and an excess of thionyl chloride. When the reaction products are evaporated off, the anhydrous chloride is obtained.

(3) *Reaction of thionyl chloride with chromic acid*

Thionyl chloride reacts quantitatively with chromium trioxide to produce chromyl chloride.

$$SOCl_2 + CrO_3 \rightarrow CrO_2Cl_2 + SO_2$$

The reagent also reacts with dry dichromates according to the reaction.

$$MCr_2O_7 + SOCl_2 \rightarrow MCrO_4 + CrO_2Cl_2 + SO_2$$

[1] J. H. FREEMAN and M. L. SMITH, *J. Inorg. Nucl. Chem.* **7**, 224 (1958).
[2] C. MOUREU, *C.R. Acad. Sci., Paris* **119**, 337 (1894).

There is no reaction with chromates, and hence the reagent provides a sensitive test to distinguish between chromates and dichromates. Thus, if the dry unknown is placed on a white tile and a drop of thionyl chloride added a transient brown colouration is obtained with dichromates since the chromyl chloride produced is soluble in the thionyl chloride. The colour can be seen with as little as 20 μg of dichromate.

(4) *Reaction of thionyl chloride with deuterium oxide*

Thionyl chloride has been used to prepare pure deuterochloric acid by reacting it with pure D_2O.[3]

It is notable that the reaction rate of liquid thionyl chloride with deuterium oxide is very much lower than its reaction rate with pure water.

An experiment at room temperature in which 1 ml of $SOCl_2$ was run from a burette into 10 ml of (a) H_2O and (b) D_2O, in open test-tubes showed that the reaction with distilled water proceeded four times more rapidly than that with heavy water. This factor is in striking contrast with that normally obtained in measurements of relative isotopic reaction rates. It seems unlikely, however, that the true reaction rates vary by such a large amount, so that the difference is probably exaggerated by physical factors controlling the size of the interface between the two reacting liquids.

The reaction of thionyl chloride with water proceeds at a high rate and is difficult to control. The reaction is exothermic with pure water but becomes endothermic when the water is saturated with HCl. It is also very temperature dependent. The reaction rate also depends upon the size of the interface between the two immiscible liquids, and this varies with the rate of gas evolution. An attempt was made to study the true reaction rate by using a solvent in which both water and thionyl chloride were soluble, thus reducing the system to a single phase, but unfortunately thionyl chloride reacts with most lyophillic solvents and the results obtained were not consistent.

Finally it is interesting to note that both polyvinyl chloride and polythene are soluble in thionyl chloride. P.V.C. dissolves on warming and the cold solution, which is quite stable, can be used for preparing films of the plastic, or for impregnating porous materials. Polythene has a low solubility at room temperature but dissolves in boiling thionyl chloride.

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C. E. C. Richards

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Didcot, Berks

[3] J. H. Freeman and C. E. C. Richards, *AERE/GP/R*-2479 (1958).

The "covalent" radius of radon and the electronegativities of gold, mercury, thallium, lead, and bismuth

(*Received* 14 *March* 1958)

The "stability ratio" method of evaluating the electronegativities of the elements[1] required the assignment of "nonpolar covalent" radii to atoms of the inert elements. These were estimated for all but radon by extrapolation of isoelectronic crystal ionic radii. Requisite data were not available to determine a radon radius, which was therefore estimated to be 2·29 Å, from the radii of krypton (1·89 Å) and xenon (2·09 Å). This corresponds to an average electronic density of 1·72 electrons/Å^3, leading to electronegativities for gold through bismuth from 3·4 to 3·8 (or, 2·3 to 2·5 on the Pauling scale[2]). Haissinsky[3] reported values (Pauling scale) diminishing from 2·3 for gold to 1·8 for bismuth. Chemically, the characteristic relative inertness of the 6*s* electron pair toward polar bond formation makes difficult any judgment of the adequacy of electronegativity values for these elements. It was certainly desirable to establish the radius of radon on a more satisfactory basis.

[1] R. T. Sanderson, *J. Chem. Educ.* **29**, 539 (1952).
[2] R. T. Sanderson, *J. Chem. Phys.* **23**, 2467 (1955).
[3] M. Haissinsky, *J. Phys. Radium* **7**, 7–11 (1946).

This is to report a new empirical approach by which has been obtained a new radon radius that in several ways seems more acceptable. The implications of this approach may be of fundamental interest.

The inert elements are found to conform to the following relationship:

$$Z^{\frac{1}{2}} = 4{\cdot}73\, n/r - 4{\cdot}00 \qquad (1)$$

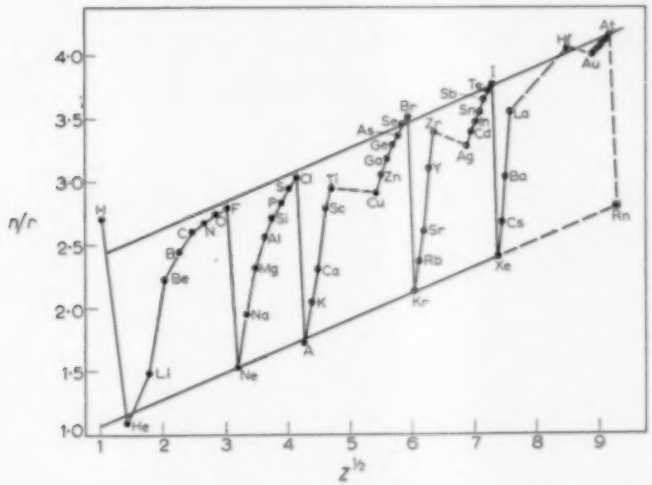

FIG. 1.

Z is the atomic number, n the principal quantum number of the outermost shell, and r the "nonpolar covalent" radius. Fig. 1 is a graph of $Z^{\frac{1}{2}}$ vs. n/r for all the elements for which appropriate radii are known. By use of equation (1), or by linear extrapolation on the graph, a radius of 2·14 Å is obtained for radon. It is very interesting that the figure is close to being a parallelogram. Indeed, the halogens are located at a practically constant distance from the nearest inert element, such that the expression,

$$n(1/r_x - 1/r_i) = 1{\cdot}34 \qquad (2)$$

can also be used to calculate the radius of radon. Here r_x is the halogen radius and r_i the inert element radius. If one may confidently extrapolate the radii of Au–Bi (1·50–1·46) to 1·44 Å for At, which seems reasonable, the radius of radon is then calculated by equation (2) as 2·12 Å.

The good agreement by these two methods suggests that the new radon radius should be preferable to the older value. The value of 2·14 corresponds to an average electronic density of 2·09. From this, interpolating between xenon and radon, revised electronegativities of gold, mercury, thallium, lead, and bismuth have been computed. These values, compared with the old and also converted to the Pauling scale for comparison with other literature values, are listed in Table 1. It would appear reasonable to replace the older values with the new ones.

TABLE 1.—ELECTRONEGATIVITIES OF Au, Hg, Tl, Pb AND Bi

	Stability ratios		Pauling scale	
	Old[1]	New	New	HAISSINSKY[2]
Au	3·39	2·83	1·89	2·3
Hg	3·47	2·93	1·92	1·9
Tl	3·58	3·02	1·96	1·9
Pb	3·67	3·06	2·00	1·8
Bi	3·78	3·14	2·05	1·8

Incidentally, the inert elements may be observed, in Fig. 1, to have, relative to their atomic numbers, the largest radius for each principal quantum number of the outermost shell. This is expected if maximum inner symmetry implies minimum interelectronic repulsion consistent with high nuclear-electronic attraction. In other words, the inert atoms may be thought of as possessing structures in which the electrons are, on the average, as far apart from one another as possible, yet still held to the nucleus as tightly as possible.

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The thermal decomposition of americium (III) oxalate

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HYDRATED americium oxalate was precipitated from a nitrate solution by a few drops of a saturated solution of oxalic acid and dried in a vacuum (1 μ) at room temperature. Americium of high purity was used; the only impurities detected were Mg(0·5), Al(0·5) and Si(0·2 per cent). The thermal decomposition of americium oxalate in air and *in vacuo*, was studied with the aid of a thermogravimetric balance. The oxalate was heated at the rate of 3°C per minute and readings were taken at 5°C intervals.

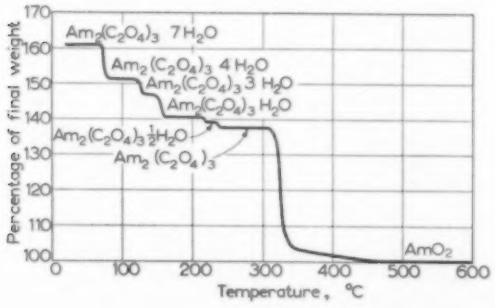

FIG. 1.—The thermal decomposition of americium oxalate in air.

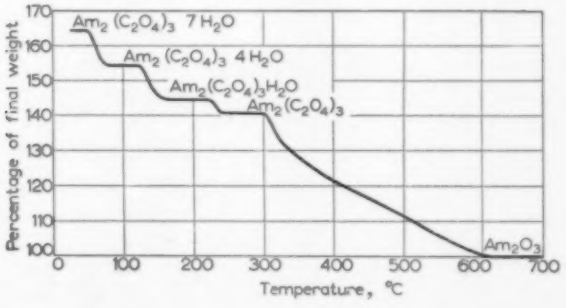

FIG. 2.—The thermal decomposition of americium oxalate *in vacuo*.

In air, the conversion of the oxalate to oxide was completed at 470°C. The reflections on the X-ray powder photograph of the final product, heated to 500°C, were broad and diffuse. However, the pattern was similar to that of AmO_2, prepared by the ignition of the nitrate or sulphate at 900°C. The oxide, prepared from the oxalate at 500°C, dissolved readily in concentrated sulphuric acid but only slowly in dilute hydrochloric acid. A number of plateaux were observed in the thermogravimetric plot and the probable compound corresponding to each plateau was calculated by assuming

the final compound to be stoicheiometric AmO_2. The results show that the oxalate, dried in a vacuum at room temperature, existed as the heptahydrate. Anhydrous americium oxalate was formed by heating the heptahydrate to 240°C. There was no evidence for the formation of a stable carbonate between the decomposition of the oxalate and formation of the oxide.

In vacuo, the heptahydrate began to lose water of hydration at 50°C. Anhydrous americium oxalate was formed at 240°C, and decomposition to the red-brown sesquioxide Am_2O_3, commenced at 290°C. The conversion of the oxalate to the sesquioxide was completed at 620°C. The plateaux corresponding to the trihydrate and demi-hydrate of americium oxalate, observed during the thermal decomposition of the heptahydrate in air, were not observed *in vacuo*. However, both of these hydrates were only stable in air over a small temperature range and it is possible that *in vacuo* the greater oscillation of the balance spiral may have obscured the observation of plateaux corresponding to the tri-hydrate and demi-hydrate.

The sesquioxide was allowed to cool *in vacuo* to room temperature and it was oxidized to AmO_2 on heating to 200°C in air.

Acknowledgements—The author wishes to thank Mr. F. T. Birks for the spectrographic analysis and Dr. E. Wait, who examined the X-ray diffraction photograph.

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The preparation of rhenium from iodo compounds

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The physical properties of metals are affected by impurities and it is therefore desirable to prepare a metal in a number of ways. Rhenium is usually prepared by hydrogen reduction of oxy-salts and by thermal decomposition of the trichloride and carbonyl.[1] Here we record a preparation by decomposition of iodo compounds.

Potassium hexaiodorhenate (IV) decomposes in vacuo at 500° mainly to potassium iodide, rhenium and iodine. At 700° potassium iodide sublimes off to leave an iodine-free product, but analyses showed retention of potassium. This cannot be ascribed to the retention of alkali as in the hydrogen reduction of potassium perrhenate, and it indicates that an unsolvated potassium rhenide is stable at high temperatures.[2]

Ammonium hexaiodorhenate (IV) prepared quantitatively from rhenium heptoxide decomposes quantitatively to rhenium at 700° *in vacuo*. A compound approximating to rhenium tri-iodide was prepared by evaporating the eluate, obtained by passing potassium hexachlororhenate in hydrochloric acid through a cation exchange column, to dryness with hydriodic acid. This iodide also decomposed to rhenium *in vacuo*. We have confirmed and extended the observations that rhenium iodides cannot be prepared by direct combination alone or in complexing and non-complexing solvents for iodine.

The hexaiodorhenates can be prepared quantitatively from the corresponding chlorides. It has been shown that the series K_2ReCl_6, K_2ReBr_6 and K_2ReI_6 can be interconverted in either direction with the appropriate halogen acids but with greater difficulty to the left. The hexachloro salt is converted to potassium perrhenate and bifluoride with hydrofluoric acid and not to the hexafluoro salt.[3] The last resembles the hexafluoro iridate and not osmate or platinate.[4]

[1] S. Tribalat, *Rhenium et Technetium*. Gauthier-Villars, Paris (1957).
[2] C. L. Rulfs and P. J. Elving, *J. Amer. Chem. Soc.* **73**, 3287, (1951); A. V. Grosse, *Z. Naturf.* **86**, 533, (1953).
[3] R. D. Peacock, *J. Chem. Soc.* 1291, (1956).
[4] A. G. Sharpe, *J. Chem. Soc.* 2444, (1950); M. A. Hepworth, P. L. Robinson and G. J. Westland, *Ibid.* 4268, (1954).

EXPERIMENTAL

Potassium hexaiodorhenate (IV). This compound was prepared from the chlorosalt, heated in a silica tube *in vacuo* (10^{-3} mm mercury) and the iodine formed collected in a cooled trap. The tube was cut to separate sublimed iodide from the residue. In a typical experiment at 700°C 665·7 mg of salt produced 204·7 mg potassium iodide, 335·8 mg iodine and 13·8 mg of residue instead of 215·4, 329·6 and 120·7 mg calculated for complete decomposition. If the 10·7 mg of unrecovered potassium iodide is distributed as KRe and iodine then the residue would weigh 123·2 and the iodine 337·8 in agreement with the osbserved values.

Rhenium tri-iodide. K_2ReCl_6 (216 mg) dissolved in 25 ml of 0·01 N hydrochloric acid was passed through a strong cation exchange resin and the eluate evaporated to dryness with hydriodic acid to give 249·4 mg of product. (Calc. for H_2ReI_6 430 mg; ReI_4, 314 mg; ReI_3 256 mg.) This was heated *in vacuo* for 2 hr at 800°C. There remained 79·2 mg of rhenium, identified by X-ray analysis, and 15·0 mg of iodine were collected. The I/Re mole ratio was 2·94. The amounts of rhenium and iodine recovered were lower than calculated probably due to the presence of an oxyiodide which could be seen as a black sublimate on the tube. The discrepancy between calculated and observed values leads to an approximate composition of $ReOI_3$ for this sublimate.

Ammonium hexaiodorhenate (IV). About 1 g of rhenium heptoxide was dissolved in water and exactly neutralized with 0·7 N ammonium hydroxide, and an identical increment added. The solution was then evaporated with excess hydriodic acid just to dryness. (Found: NH_4, 3·56%; product/Re_2O_7, 4·065. Calc. NH_4, 3·66%; $(NH_4)_2ReI_6/\frac{1}{2}Re_2O_7$, 4·060).

A quantity, 195·6 mg, of this salt as heated *in vacuo* at 700°C for 4 hr to yield 98·8 mg iodine, 57·6 mg ammonium iodide and 37·0 mg rhenium compared with the calculated 101·0, 57·6 and 37·0 mg respectively.

An attempt was made to isolate an intermediate simple iodide by heating at 250°C for a few days. The weight decreases linearly with time until the weight loss is approximately equal to the amount of ammonium iodide in the sample. The rate of loss then increases sharply but there was no inflexion at the composition corresponding to the tri-iodide. Analysis also indicates that ammonium iodide is removed preferentially. Thus after 5 hr at 300°C the ratio I/NH_4I evolved is 1·1 instead of 2·0 for uniform decomposition. A careful thermogravimetric analysis should reveal the presence of simple iodides.

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Thallous 12-molybdophosphate

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In a previous communication[1] we showed that the ammonium in ammonium 12-molybdophosphate (AMP) could be partly replaced by the heavier alkali metal cations and by thallous ions from acidified and neutral solutions. About 2 moles of thallium were taken up per mole of AMP, whilst only 1 mole of alkali metal was exchanged under the given conditions. In view of this, it seemed of interest to prepare precipitates of thallous 12-molybdophosphate (TlMP) and to compare them with the 12-molybdophosphates of potassium, rubidium, caesium and ammonium.

[1] H. Buchwald and W. P. Thistlethwaite, *J. Inorg. Nucl. Chem.* **5**, 341 (1958).

Apart from the observation by FINKENER[2] that TlMP is the least soluble of all the 12-molybdophosphates, and the demonstration by ILLINGWORTH and KEGGIN[3] that it has a similar structure to the other salts, little work appears to have been done on this compound.

THISTLETHWAITE'S[4] method for the preparation of AMP, in which the 12-molybdophosphate ion

TABLE 1.—CONDITIONS FOR THE PRECIPITATION OF 12-MOLYBDOPHOSPHATES FROM SOLUTIONS OF 12-MOLYBDOPHOSPHORIC ACID

No.	Cation	In solution			Ratio $\frac{[\text{cation}]}{[\text{anion}]}$ found in precipitate
		Moles of cation (per litre)	Ratio $\frac{[\text{cation}]}{[\text{anion}]}$	Ratio $\frac{[\text{cation}]}{[H^+]}$	
1	Tl^+	0·0049	0·773	0·0032	2·17
2	Tl^+	0·0049	0·773	0·0032	2·20
3	Tl^+	0·0047	2·45	0·0058	3·05
4	Tl^+	0·0047	2·45	0·0058	3·02
5	Tl^+	0·0489	28·30	0·236	3·42
6	Tl^+	0·0489	28·30	0·236	3·37
7	Tl^+	0·0489	28·30	0·236	3·26
8	Tl^+	0·0489	28·30	0·236	3·38
9	Tl^+	0·0489	28·30	0·236	3·18
10	Tl^+	0·0489	28·30	0·236	3·22
11	Tl^+	0·0489	28·30	0·236	3·49
12	Tl^+	0·0489	28·30	0·236	3·43
13	Tl^+	0·0489	28·30	0·236	—
14	Tl^+	0·0489	28·30	0·236	—
15	Tl^+	0·0489	28·30	0·236	3·27
16	Tl^+	0·0577	33·40	0·041	4·14
17	Tl^+	0·0577	33·40	0·041	4·42
18	Tl^+	0·0657	137·0	0·858	3·96
19	Tl^+	0·0657	137·0	0·858	3·37
20	Cs^+	0·0489	28·20	0·237	2·09
21	Cs^+	0·0489	28·20	0·237	2·08
22	Rb^+	0·0049	28·30	0·237	2·20
23	Rb^+	0·0049	28·20	0·237	2·20
24	K^+	0·0490	28·30	0·237	1·82
25	K^+	0·0925	29·50	1·960	2·04
26	K^+	0·1930	30·40	1·980	2·05
27	NH_4^+	0·0490	29·10	0·243	2·36
28	NH_4^+	0·0490	29·10	0·243	2·11

is formed from acidified solutions of phosphate and molybdate in the presence of the cation, can be used to prepare the potassium, rubidium and caesium salts (though quantitative yields are not obtainable owing to their greater solubility). This method cannot be used to prepare TlMP because thallous molybdate is insoluble under the given conditions and preferentially precipitated. An alternative method was evolved in which thallous nitrate solution was added, with continuous

[2] R. FINKENER, *Ber. Dtsch. Chem. Ges.* **11**, 1638 (1878).
[3] J. W. ILLINGWORTH and J. F. KEGGIN, *J. Chem. Soc.* 575 (1935).
[4] W. P. THISTLETHWAITE, *Analyst* **72**, 531 (1947).

stirring, to a heated (50°C) solution of A.R. 12-molybdophosphoric acid. The fine yellow precipitates of TlMP were prepared by this method using various cation–12-molybdophosphoric acid ratios. Other 12-molybdophosphates were prepared in a similar manner for comparison. The precipitates were carefully washed and dried to constant weight at 130°C; some were analysed for the cation, molybdenum and co-precipitated nitrate, whilst others were sent for X-ray powder photographs. Base exchange[1] with ammonium ions was attempted on two of the TlMP precipitates by treatment with a solution of ammonium nitrate (0·1 M) in nitric acid (0·08 M).

TABLE 2.—12-MOLYBDOPHOSPHATES PREPARED BY THISTLETHWAITE'S METHOD

Cation	In solution			Ratio $\frac{[\text{cation}]}{[\text{anion}]}$ found in precipitate
	moles of cation (per litre)	Ratio $\frac{[\text{cation}]}{[\text{anion}]}$	Ratio $\frac{[\text{cation}]}{[\text{H}^+]}$	
Cs^+	0·340	218	0·24	2·45
Cs^+	0·340	218	0·24	2·58
Rb^+	0·331	212	0·24	2·48
Rb^+	0·284	182	0·23	2·39
Rb^+	0·331	264	0·23	2·48
NH_4^+	0·338	218	0·24	2·54
NH_4^+	0·338	218	0·24	2·54

Results

Table 1 shows the cation–anion ratios found in precipitates of TlMP prepared by using varying quantities of Tl^+ and $[PMo_{12}O_{40}]^{3-}$. The table also shows the results for other 12-molybdophosphates prepared under similar conditions.

No figures are given in the last column for numbers 13 and 14, since these samples were not analysed, but chosen as being representative of the set, and sent for X-ray powder photographs. Numbers 5, 6 and 8 were also examined for co-precipitated thallous nitrate by analysing for nitrate. A small amount of nitrate was found present in each case, and allowing for this, the respective cation–anion ratios were reduced to 3·15, 3·13 and 3·05.

Base exchange with ammonium ions was attempted with precipitates 11 and 12, after which they showed the following thallium distribution:

	No. 11	No. 12
Tl in exchanged precipitate	3·04	3·01
Tl in exchange effluent	0·45	0·42
(all per mole of anion)		
Total Tl	3·49	3·43

Table 2 shows results obtained in preparing various 12-molybdophosphates using THISTLETHWAITE'S[1] method.

Discussion

Although the lower solubility of thallous salts restricts the range of concentrations that can be studied, when compared with other cations, the results suffice to show that thallium (I) behaves towards 12-molybdophosphoric acid quite differently from the other cations studied.

Under all the conditions examined, the 12-molybdophosphates of ammonium, potassium, rubidium and caesium are acid salts containing from 1·82 to 2·58 moles of cation per mole of anion. Even when the cation–anion ratio in solution was very high (218 : 1), the normal salts did not appear. Thallium offers a marked contrast to this behaviour, the cation–anion ratio appearing to be a less important factor. All the precipitates examined, except numbers 1 and 2, were "normal" salts

containing at least three atoms of thallium per anion even where the ratio in solution is only 2·45 : 1 (Nos. 3 and 4), and therefore an acid salt might be expected. An unexpected feature of the results is the indication that more than three thallous ions may be present in the compound.

It is evident that the TlMP prepared is a compound of exceptional stability and insolubility, and that additional thallium can be taken up. It is obviously inappropriate to speak of a basic salt in the acid conditions prevailing in the mother liquor (pH $< 1{\cdot}5$). The base exchange experiments, taken in conjunction with those reported in [1] also indicate that thallous ions are held more tenaciously than the other univalent cations. The fact that TlMP is much less soluble than the rubidium and ammonium salts (although all these ions have approximately the same size) indicates that thallium is able to distort the anion structure by polarization.

The X-ray examination of numbers 13 and 14 and samples of the potassium, rubidium and caesium salts were undertaken to discover whether this apparently stronger bonding was reflected in a change of structure. No indication of such a difference was found, all the patterns being those of a cubic lattice of cell edge about 11·7 Å ($\pm 0{\cdot}5$) and very similar to that of 12-molybdophosphoric acid itself. There were, however, small differences between the different photographs, such as might be caused by changes in the scattering factors of different cations, or by some change in the number and position of the cations.

Conclusions

Thallous 12-molybdophosphate is a normal salt containing three (or slightly more) thallous ions and is of exceptional stability and insolubility. The stability was confirmed by the evidence of base exchange experiments, where thallium competes successfully with all other univalent cations, including ammonium. In contrast to the salts of ammonium, potassium, rubidium and caesium, there is little tendency towards the formation of acid salts, even under very acidic conditions. X-ray analysis shows no positive evidence of any structural differences.

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Complex cyanides involving metal–metal bonds

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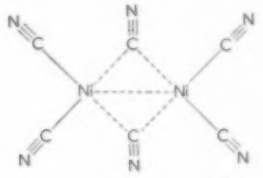
There are two transition metal binuclear complex cyanides, the structures of which are still matters of discussion. The first, $K_4[Ni(CN)_3]_2$ is produced by reduction of potassium tetracyanonickelate $K_2[Ni(CN)_4]$ by potassium in liquid ammonia;[1] it is diamagnetic,[2] dimeric[3] and has been shown[4] to contain monovalent nickel. With nitric oxide and carbon monoxide it forms the diamagnetic complexes $K_2[Ni(CN)_3NO]$[5] and $K_2[Ni^{I}(CN)_3CO]$;[6] the latter must be a dimer to explain the diamagnetism.

[1] I. Bellucci and R. M. Coulli, *Atti R. Accad. Lincei* **22**, ii 485 (1913).
[2] D. P. Mellor and D. P. Craig, *Proc. Roy. Soc. N.S.W.* **76**, 281 (1942).
[3] R. Nast and W. Pfab, *Naturwissenschaften* **39**, 300 (1952); *Z. Naturf.* **126**, 122 (1957).
[4] D. N. Hume and I. M. Kolthoff, *J. Amer. Chem. Soc.* **72**, 4423 (1950); V. Caglioti, G. Sartori and P. Silvestroni, *Atti Accad. Natl. Lincei, Classe Sci. Fis. Mat. Nat.* **3**, 448 (1947); A. A. Vlček, *Chem. Listy* **50**, 1072 (1956); **50**, 1416 (1956); [In English: A. A. Vlček, *Coll. Czechoslov. Chem. Commun.* **22**, 948 (1957); **22**, 1736 (1957)].
[5] R. Nast, *Z. Anorg. Chem.* **256**, 145 (1948).
[6] R. Nast and T. von Krakkay, *Z. Anorg. Chem.* **272**, 233 (1953); W. P. Griffith, F. A. Cotton and G. Wilkinson, *J. Amer. Chem. Soc.* In press.

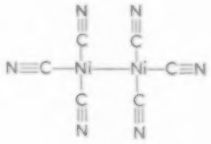
The second complex, $K_6[Co(CN)_5]_2$ is also diamagnetic in the solid state[7,8] and contains divalent cobalt;[9] in solution it has been shown to exist as the paramagnetic species $[Co(CN)_5H_2O]^{3-}$.[9]

Infra-red studies on $K_4[Ni(CN)_3]_2$ and $K_2[Ni(CN)_4]$ have been previously reported.[10] We have repeated these measurements and in addition have measured the spectra of $K_2[Ni(CN)_3NO]$, $K_6[Co(CN)_5]_2$ and of other cobalt cyano complexes.

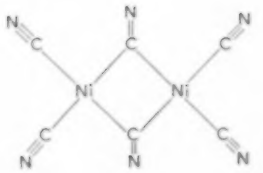
There have been three structures (I–III) previously proposed for $K_4[Ni(CN)_3]_2$. Although a preliminary X-ray examination of this compound, indicating a dimeric structure with cyanide bridges, has been reported[3] several years ago, no further details have been published. Accepting the correctness of the presence of bridging cyanide groups, (which cannot however be considered as being



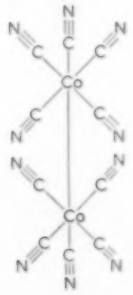
I



II



(III)



IV

unequivocally proved), and since no cyanide frequencies displaced to low wave numbers (as occurs with carbon monoxide in the bridging position in binuclear carbonyls) were observed, EL-SAYED and SHELINE[10] were required to make the unusual and rather *ad hoc* assumption that the highest band of the three observed in the cyanide C≡N stretching region (at 2130 cm^{-1}) was attributable to the bridging cyanide group bound to the nickel atom by half-bonds (structure I). We find, however, that all of the nickel and cobalt complexes have an intense absorption in the region 2135 cm^{-1}. Since, with the exception of $K_4[Ni(CN)_3]_2$, $K_4[Ni(CN)_3CO]_2$ and $K_6[Co(CN)_5]_2$, these are necessarily monomeric, it seems to us much more reasonable to attribute absorption in the 2135 cm^{-1} region to terminal cyanide groups. In the absence of conclusive X-ray evidence to the contrary, we must therefore conclude that both $K_4[Ni(CN)_3]_2$ and $K_6[Co(CN)_5]_2$ contain metal–metal bonds brought about by spin coupling of the unpaired electrons on the nickel and cobalt atoms respectively. The MELLOR and CRAIG[3] structure (II), with point group D_{2h}, in which all the six CN groups and the two nickel atoms are coplanar, would, as pointed out by EL-SAYED and SHELINE, give rise to three infra-red active C≡N frequencies, as observed. It was also pointed out that this structure is energetically most feasible. A similar structure (IV) (point group D_{4d} or D_{4h}) for $K_6[Co(CN)_5]_2$, which also has three strong C≡N stretches can be formulated; the structure can be considered analogous to that of $Re_2(CO)_{10}$, for which three CO stretching frequencies have been observed[11,12] and for which single-crystal X-ray studies[13] have conclusively shown D_{4d} symmetry and the presence of a

[7] A. W. ADAMSON, *J. Amer. Chem. Soc.* **73**, 5710 (1951).
[8] L. SZEGO and P. OSTINELLI, *Gazz. Chim. Ital.* **60**, 946 (1930).
[9] D. N. HUME and I. M. KOLTHOFF, *J. Amer. Chem. Soc.* **71**, 867 (1949).
[10] M. F. EL-SAYED and R. K. SHELINE, *J. Amer. Chem. Soc.* **78**, 702 (1956).
[11] F. A. COTTON, A. LIEHR and G. WILKINSON, *J. Inorg. Nucl. Chem.* **2**, 141 (1956).
[12] E. O. BRIMM, M. A. LYNCH JR. and W. J. SESNY, *J. Amer. Chem. Soc.* **76**, 3831 (1954).
[13] C. F. DAHL, E. ISHISHI and R. E. RUNDLE, *J. Chem. Phys.* **26**, 1750 (1957).

metal–metal bond. The D_{4d} configuration for the $[Co_2(CN)_{10}]^{6-}$ ion is more likely, although the infra-red measurements would not exclude D_{4h}, since VAN DER WAALS forces would favour a staggered configuration as in the rhenium and manganese carbonyls. This also applies to the $[Ni_2(CN)_6]^{4-}$ ion which could also have symmetry D_{2d}.

The peak at 1780 cm^{-1} in $K_2[Ni(CN)_3NO]$ clearly arises from absorption in a co-ordinated nitrosyl (NO^+) group, and this, together with the known diamagnetism, confirms its C_{3v} configuration which is similar to that of $Co(CO)_3NO$.[14]

EXPERIMENTAL

The complexes were made and purified according to the following references: $K_2[Ni(CN)_4]$[15] (K calc., 32·45; found: 32·18%); $K_4[Ni(CN)_5]_2$[16] (K calc., 40·10; found: 39·08%); $K_2[Ni(CN)_3NO]$[13] (K calc., 31·93; found: 32·38%); $(K_2[Co(CN)_6]$[17] (K calc., 35·90; found: 35·69%); $K_6[Co(CN)_5]_2$[17] (K calc., 39·10; found: 39·01%); $K_3[Co(CN)_5(OH)]H_2O$[18] (K calc., 34·36; found: 33·56%); $K_2[Co(CN)_5NO].2H_2O$[19] (K calc., 31·53; found: 31·99%).

Infra-red spectra

Infra-red spectra were taken in Nujol mulls using a Perkin-Elmer Model 21 spectrophotometer with sodium chloride optics.

Complex	C≡N stretches	NO stretches
$K_2[Ni(CN)_4]$	2136*vs*	
$K_4[Ni(CN)_5]_2$	2131*vs*; 2083*vs*; 2061*vs*	
$K_2[Ni(CN)_3NO]$	2133*vs*; 2118*vs*	1780*vs* (NO^+)
$K_2[Co(CN)_4]$	2143*vs*	
$K_6[Co(CN)_5]_2$	2133*vs*; 2090*vs*; 2079*vs*	
$K_3[Co(CN)_5OH].H_2O$	2135*vs*; 2114*w*,*sh*	
$K_2[Co(CN)_5NO].2H_2O$	2141*vs*; 2104*w*, *sh*	1120*m* (NO^-)

Acknowledgement—One of us (W. P. G.) is indebted to the Department of Scientific and Industrial Research for financial support.

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Imperial College, London

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The acid strength of triphenylsilanol

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ON the basis of the magnetic resonance shielding observed for the hydroxyl proton of trimethylsilanol and *tert*-butyl alcohol, ALLRED[1] has proposed that silanols generally may be more acidic than alcohols with analogous structures. The enhanced acidity of silanols is presumed to arise from d_π–p_π

[1] L. ALLRED, E. G. ROCHOW and F. G. A. STONE, *J. Inorg. Nucl. Chem.* **2**, 416 (1956).

bonding between oxygen and silicon. Our recent work on the strength of hydrogen bonding in mixtures of bases with silanols and with carbinols substantiates ALLRED's suggestion.[2] As hydrogen bonding acids, silanols are markedly stronger than the analogous carbinols. Particularly great acidity was found for aryl silanols; in hydrogen bond formation triphenylsilanol behaves as an acid *at least as strong as phenol*.

This surprising observation suggested that triphenylsilanol might be titrated as a weak acid. Because of the insolubility of triphenylsilanol and its salts, such a titration cannot be carried out in water. We find, however, that this compound may be titrated in pyridine solution, using tetrabutyl ammonium hydroxide in benzene–methanol as titrant.[3] Visual titration using alizarin yellow as an indicator gives analyses accurate to within ± 2 per cent. Accurate determinations can also be obtained by potentiometric titration using glass vs. methanol-modified calomel electrodes.[3]

The half-neutralization values obtained in potentiometric titration give the first direct measure of the Brønsted acidity of a silanol compared to other weak acids. We find the following reproducible half-neutralization voltages: phenol, 0·68; *p*-methoxyphenol, 0·73; triphenylsilanol, 0·80; *p*-nitroaniline, 0·90, all $\pm 0{\cdot}01$ v., at 0·01 to 0·02 M. Triphenylsilanol is therefore somewhat weaker as a protonic acid than most phenols, but somewhat stronger than *p*-nitroaniline. Triphenylsilanol must also be far stronger than trialkylsilanols or alkyl or aryl carbinols, since these classes of compounds are all too weak to be titrated in the system used. It should therefore be possible to determine triphenylsilanol in the presence of carbinols and alkylsilanols by this titration method.

The titration described above may be useful both for the analytical determination of aryl silanols, and as a tool in studying the influence of electronic factors on pi-bonding in silicon compounds. The potentiometric titration of other aryl silanols is now under intensive study.

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The preparation of a solution of plutonium(V) in 0·2 M HNO_3

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A SOLUTION containing plutonium in the pentavalent state only has been prepared by mixing equal concentrations of Pu(III) and Pu(VI) in 0·2 M HNO_3 in the presence of dibutyl phosphate in benzene. The equilibrium for the following reaction is rapidly attained

$$Pu(III) + Pu(VI) \rightleftharpoons Pu(IV) + Pu(V)$$

and may be shifted to the right by removal of Pu(IV) by the organic solvent.

A solution of Pu(IV) (2 mg/ml) in 0·2 M HNO_3 solution was divided into two equal portions. One portion was oxidized electrolytically to Pu(VI) and the second portion was reduced by sulphur dioxide gas to Pu(III). Excess SO_2 was removed by bubbling nitrogen through the solution for 3 hr. Pu(III) and Pu(VI) were mixed together and stirred in the presence of 0·1% D.B.P. in benzene. Pu(IV) was extracted into D.B.P. leaving Pu(V) in the aqueous phase. There was a tendency towards emulsion formation in the aqueous phase but this was overcome by decreasing the rate of stirring. The extraction of Pu(IV) was completed in 15 min. Spectrophotometric measurements using a Hilger Uvispek Spectrophotometer showed that only Pu(V) existed in the aqueous phase. The disproportionation of Pu(V) in 0·2 M acid solution is slow[1] and no other valency of plutonium in the aqueous phase was observed during the spectrophotometric measurements.

[1] R. E. CONNICK, *Radiochemical Studies: The Fission Products* Vol. 14B, Paper 3.18 (Edited by N. SUGARMAN and C. D. CORYELL) NNES, Plutonium Project Record. McGraw-Hill, New York (1951).

An aqueous solution of Pu(V) has also been obtained by extraction of Pu(IV), formed in the equilibrium reaction, into 0·07% D.B.P. in dibutyl ether. A cloudiness appeared in the aqueous phase after several hours, probably due to some dibutyl ether remaining in this phase and undergoing decomposition to peroxides.

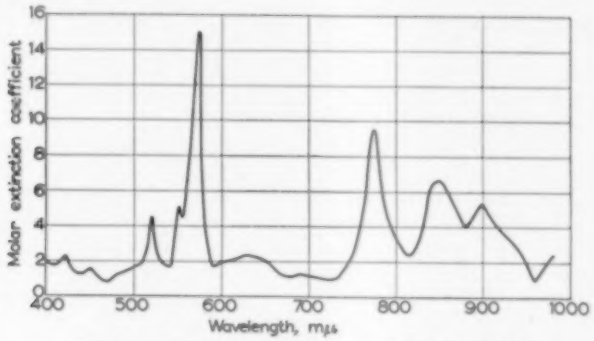

FIG. 1.—Absorption spectrum of Pu(V) in 0·2 M HNO_3.

The preparation of a solution of Pu(V) by the extraction of Pu(IV) into T.T.A. was investigated but the extraction is slower than into D.B.P. and an observable disproportionation of Pu(V) in the aqueous phase had occurred by the time spectrophotometric measurements were made.

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Use of sparingly-soluble salt-forming reagents as eluting agents in cation-exchange processes

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COMPLEXING agents have been widely used to remove multivalent metal cations from cation-exchangers. A complexing agent such as an anion of an organic acid reduces the distribution coefficient of a metal between the resin and the solution phase by converting a considerable part of the metal cation in the solution into less adsorbable species, i.e., anionic, neutral and less positively charged cationic species. Any reagent that decreases the thermodynamic activity of the metal cation in the solution would also have the same effect as that of a complexing agent. Reagents that form sparingly soluble salts with the cation to be removed were therefore examined as to their suitability as eluting agents. In every case tested, the reagent was proved to be effective, and in some cases the reagents were found to be of practical use.

As an example, we shall demonstrate that the perchlorate ion promotes elution of the caesium ion. Experiments were carried out as a part of the study on ion-exchange separation of fission products. A solution of aged gross fission products in 0·2 N HCl, which was prepared from their nitric acid solution supplied by the Atomic Energy Commission, U.S.A., was used as the sample solution containing caesium-137; the other components did not affect the behaviour of caesium-137. The column was 8 mm dia. and 50 mm long, and contained 3·7 mequiv of Dowex 50 X8 (hydrogen form) of 100–200 mesh. After adsorption of the caesium ion (together with the other cations) on the top of the column and washing the column with 15 ml of 0·2 N HCl, the caesium ion was eluted with 1 N $HClO_4$. The maximum caesium activity was found in the seventh millilitre portion of the

effluent, compared with the eleventh or the fifteenth portion in the case of elution with nitric or hydrochloric acid. A similar effect was also observed when 0·5 N acids were used as eluents; i.e., the maximum of the caesium activity was located at the twenty-sixth, thirty-third and thirty-seventh millilitre portion for elution with perchloric, nitric and hydrochloric acid, respectively. When ammonium salts were used instead of free acids, the appearance of the caesium in the effluent was delayed until all the cation-exchanger was converted into the ammonium form. With 1 N ammonium perchlorate, elution of the caesium took place immediately after the conversion of the exchanger, whereas with 1 N ammonium sulphate it was further delayed by several column volumes.

Such experimental results may be explained as follows. In view of the low solubility of caesium perchlorate, it is very likely that the caesium ion has a marked tendency to form some kind of aggregate with the perchlorate ion. Irrespective of the nature of the aggregate produced, the thermodynamic activity of the caesium ion would decrease. Extra reduction of the thermodynamic activity of the caesium ion by the perchlorate ion might also be expected from activity-coefficient data. According to the available data,[1] the activity coefficient of potassium perchlorate in 0·02 N solution at 25° is 0·826, whereas those of potassium chloride, sodium chloride and sodium perchlorate are 0·855, 0·863 and 0·855, respectively. The activity coefficient of caesium perchlorate is expected, though the datum is not available, to be still lower than that of the potassium salt. The lower activity of the caesium ion in the solution would therefore also promote the removal of the caesium ion from the cation-exchanger.

Experiments were also performed to confirm the effectiveness of nitric acid for elution of strontium and barium, of ammonium and sodium carbonate for elution of rare-earths and strontium, and of ammonium sulphate for elution of strontium. The results and their probable explanation were parallel to the case of caesium described above.

Many reagents of this kind are useful for the treatment of carrier-free radioactive isotopes or micro quantities of substances, but they are unfavourable for the treatment of macro quantities of substances on account of the formation of precipitates, which prevents rapid elution. On the other hand, some of them, an example of which is nitric acid as the eluting agent for strontium and barium, are useful for treatment of any amount of the substance, since the solubility of the salt in question is moderately low.

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NOTE

On the preparation of iodine pentafluoride

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IT has been suggested that iodine pentafluoride was first prepared by KAMMERER in 1862,[1] but this was actually the first preparation of the heptafluoride and not of the pentafluoride.[2] Iodine pentafluoride was first prepared in 1871 by GORE[3] from silver fluoride and iodine. RUFF suggested the use of cobalt trifluoride.[4] The formation of iodine pentafluoride by the action of iodine on ruthenium pentafluoride has been described.[5] RUFF and GENREL described the vigorous action of iodine on bromine pentafluoride.[6] The action of fluorine on iodine pentoxide gives the pentafluoride[7] but the reaction is rapid only above 250°C. Iodine reacts more readily with bromine trifluoride, whilst iodates also react with bromine trifluoride[9] and in particular manganous iodate reacts vigorously with liquid bromine trifluoride.[10] Iodine reacts easily with chlorine trifluoride to form iodine pentafluoride.[11] The reaction of dry iodine with fluorine was described by several authors.[12–20]

Qualitative observations on the reaction between bromine trifluoride and oxides were made by RUFF and his co-workers.[6,21] Oxygen was found to be evolved, but a quantitative study of these reactions has shown that the reactivity of bromine trifluoride was over-emphasized, since for only twelve of the twenty-eight oxides examined was oxygen evolution complete. Certain of the quantitative reactions, as suggested by EMELÉUS and WOOLF[9] may be of service in determining the heats of formation of bromine trifluoride. They have suggested the reaction between iodine pentoxide and bromine trifluoride, which may be used in determining the heat of formation of iodine pentafluoride. No details of the above reaction were given, nor was the isolation or yield of iodine pentafluoride described.

In the course of our work we have found the reaction between iodine pentoxide and liquid bromine trifluoride

$$6I_2O_5 + 20BrF_3 = 12IF_5 + 10O_2 + Br_2$$

to be a suitable laboratory preparative method for the preparation of iodine pentafluoride. The

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[20] W. C. SCHUMB and G. A. LYNCH, *Industr. Engng. Chem.* **42**, 1383–6 (1950).
[21] O. RUFF and A. BRAIDA, *Z. anorg. Chem.* **214**, 91 (1933).

reaction can be performed in a silica flask and no special equipment is needed. The yield of the isolated pure iodine pentafluoride is about 80 per cent, although the reaction is nearly quantitative. Some material is dissolved in the bromine formed as a by-product of the reaction and consequently is lost. For the amount involved it is not worth separating.

In a similar way we have found that liquid chlorine trifluoride reacts with iodine pentoxide.

$$6I_2O_5 + 20ClF_3 = 12IF_5 + 10O_2 + 10Cl_2$$

The purification of the product in this case can be accomplished readily as the volatile chlorine evolved in the reactions is easily removed. The lower melting point of chlorine trifluoride makes it possible to work at a convenient low temperature and at the same time control the heat of reaction.

EXPERIMENTAL*

Reaction of bromine trifluoride with iodine pentoxide

In a fused silica flask 137 g (1·0 mol) bromine trifluoride was cooled to −40°C. To solid fluoride, 100·2 g (0.3 mol) iodine pentoxide was added in small portions, the mixture being shaken continuously. Contact with atmospheric moisture was avoided. Because of the great velocity of the reaction (strong oxygen evolution is also observed) in the first stage only 1 g quantities of the pentoxide are added at one time and after the addition of each portion the reaction mixture is allowed slowly to melt until the reaction is completed. As the reaction progresses the velocity decreases and 2–4 g quantities of the pentoxide may be added at once.* After adding the whole quantity of iodine pentoxide the reaction mixture is allowed to stand for an hour at +20°C, during which the whole pentoxide is dissolved and the reaction is completed. The reaction mixture is thereafter separated in a normal glass separatory funnel (during a rapid separation no measurable corrosion of the glass is observed). The lower phase is the bromine formed in the reaction, the upper the iodine pentafluoride. The separated iodine pentafluoride phase is a clear, slightly yellow liquid. Bromine contamination is less than 0·2 per cent I% calc. 57·18: found 58·84; F% calc. 42·82: found 42·60. It can be used for most purposes without any further purification. Yield 107 g (80·8 per cent). If further purification is needed a vacuum distillation can be effected. $bp_{15} = 15–17°C$.

Reaction of chlorine trifluoride with iodine pentoxide

To 46·2 g (0·5 mol) chlorine trifluoride, cooled to −50°C in a silica flask, 50 g (0·15 mol) iodine pentoxide was added in small portions with stirring (teflon covered magnetic stirrer) and avoiding air moisture. The reaction is very vigorous at first but later becomes smooth, and the temperature can be raised to −10°C. After addition of the iodine pentoxide is completed the reaction mixture is slowly warmed to room temperature. During this time the greater part of the retained chlorine is evaporated and a clear yellow liquid remains, which after distilling ($bp_{15} = 15–17°$) yields 62 g iodine pentafluoride. Yield 93·1 per cent.

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* As bromine and chlorine trifluoride reacts vigorously with water, organic materials, metals etc., during all operations these materials must be handled with adequate care as it is generally used in work with potential fluoro-chemicals. Fluorocarbon stopcock greases are recommended for all lubrications, as ordinary stopcock greases are attacked and not to be used.

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Papers to be published in future issues

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NUCLEAR THERMODYNAMICS OF THE HEAVIEST ELEMENTS—II*

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Abstract—The masses of the isotopes of the heaviest elements have been calculated from known decay data in the region, extended by means of decay energies calculated from closed decay–energy cycles and estimated from the systematics of α- and β-decay energies. The absolute values of the masses are based on the mass-spectrometrically determined mass of ^{206}Pb and a few measured neutron binding energies. The half-life systematics of α-decay and spontaneous fission are also presented, and some predictions of the properties of as yet undiscovered nuclides are made.

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A TABLE of isotopic masses is useful in calculating the energy released or absorbed in nuclear reactions and for searching for systematic trends which may produce some insight into nuclear structure. This paper presents such a table for the *trans*-thallium region along with measured, calculated, and estimated decay energies and nucleon binding energies. A summary of the energy and half-life systematics of the radioactive decay of the heaviest elements is also included.

Although compilations of this type have been published previously,[1,2] sufficient new data are available to make it advisable to recalculate the masses of the heaviest isotopes. This paper is based on data published or otherwise available to the authors up to December 1957.

DECAY ENERGIES

A. *Closed cycles*

The *trans*-thallium region is unique in that the general occurrence of alpha decay allows one to construct *closed decay–energy cycles* containing two α-decay energies and two β-decay energies. As an example, the cycle‡ ^{235}U–^{239}Np–^{243}Cm is given in Fig. 1. We observe that ^{239}Np can decay to ^{235}U by two paths. It can decay to ^{239}Pu by emitting a β-particle of 0·73 MeV. The ^{239}Pu then decays to ^{235}U by emitting a 5·24 MeV α-particle. Alternatively, ^{239}Np can α-decay to ^{235}Pa, which can then decay to ^{235}U by emitting a 1·40 MeV β-particle. The partial β-half-life of ^{239}Np is so short that the α-decay has not been observed. We can calculate the α-decay energy, however, since the total energy released in the two alternative processes

* Based on a thesis submitted by B. M. FOREMAN, JR. in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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‡ A closed cycle can be uniquely specified by giving two diagonal members. The extension to double cycles such as the one appearing in Fig. 1 is obvious.

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1

must be the same. Thus we obtain*

$$Q_\alpha(^{239}\text{Np}) = 0{\cdot}73 + 5{\cdot}24 - 1{\cdot}40 = 4{\cdot}57 \text{ MeV}.$$

From the other cycle in Fig. 1 the electron-capture decay energy of ^{243}Cm is readily calculated to be 0·00. This means that neutral atoms of ^{243}Cm and ^{243}Am have the same mass within the precision of the data used in the cycles.

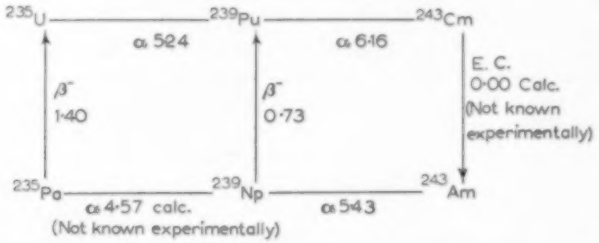

FIG. 1.—Closed cycle ^{235}U–^{239}Np–^{243}Cm. Decay energies in MeV.

These cycles can be extended by adding neighbouring cycles until the entire *trans*-thallium region is covered. However, since the cycles connect only nuclides differing in mass number by four, there will be four such sets of closed cycles, corresponding to the mass types $4n$, $4n + 1$, $4n + 2$, and $4n + 3$. The complete sets of cycles, containing all measured, calculated, and estimated decay energies in the *trans*-thallium region, are given in Figs. 2–5. In these figures the existence of isomers is denoted by the symbol †. In general, decay energies associated with the ground-state isomer have been used in the cycles. Exceptions are discussed in Appendix III.

B. *Energy systematics*

α-Decay. The regularities in α-decay energy systematics are well known[3] and are best shown in a plot of α-disintegration energy versus mass number, such as appears in Fig. 6. One of the most striking features of this graph is the regular decrease in decay energy with increasing mass number for the isotopes of a given element. Two prominent exceptions to this rule are evident. These are the large discontinuity corresponding to the 126-neutron closed shell and the smaller irregularity associated with the postulated closed subshell at 152 neutrons.[4] The 152-neutron irregularity has been observed in the curves for the elements berkelium through fermium. The curves for the other elements have been drawn with approximately the same shape, with the effect diminishing for the heavier elements. A slight dip is apparent in the curves for uranium, plutonium, and curium at 145 neutrons. This dip has been included in the estimated curves for other elements, also diminishing for heavier elements.

The estimated α-decay energies appearing in Figs. 2–5 were taken from this plot by interpolation or extrapolation. Some of the points for the elements above fermium were obtained by extrapolating lines of constant neutron number.

* Q_α is defined as the total energy released in α-decay = α-particle energy + recoil energy of residual nucleus.

[3] I. PERLMAN, A. GHIORSO and G. T. SEABORG, *Phys. Rev.* **77**, 26 (1950).

[4] A. GHIORSO, S. G. THOMPSON, G. H. HIGGINS, B. G. HARVEY and G. T. SEABORG, *Phys. Rev.* **95**, 293 (1954).

FIG. 2.—Closed decay–energy cycles for the $4n$ series: No superscript, measured energy; *c*, calculated; *cn*, calculated with neutron binding energies; *e*, estimated; *ce*, calculated from a cycle containing estimated energies; ( ), uncertain by more than about 0·1 MeV; †, isomers.

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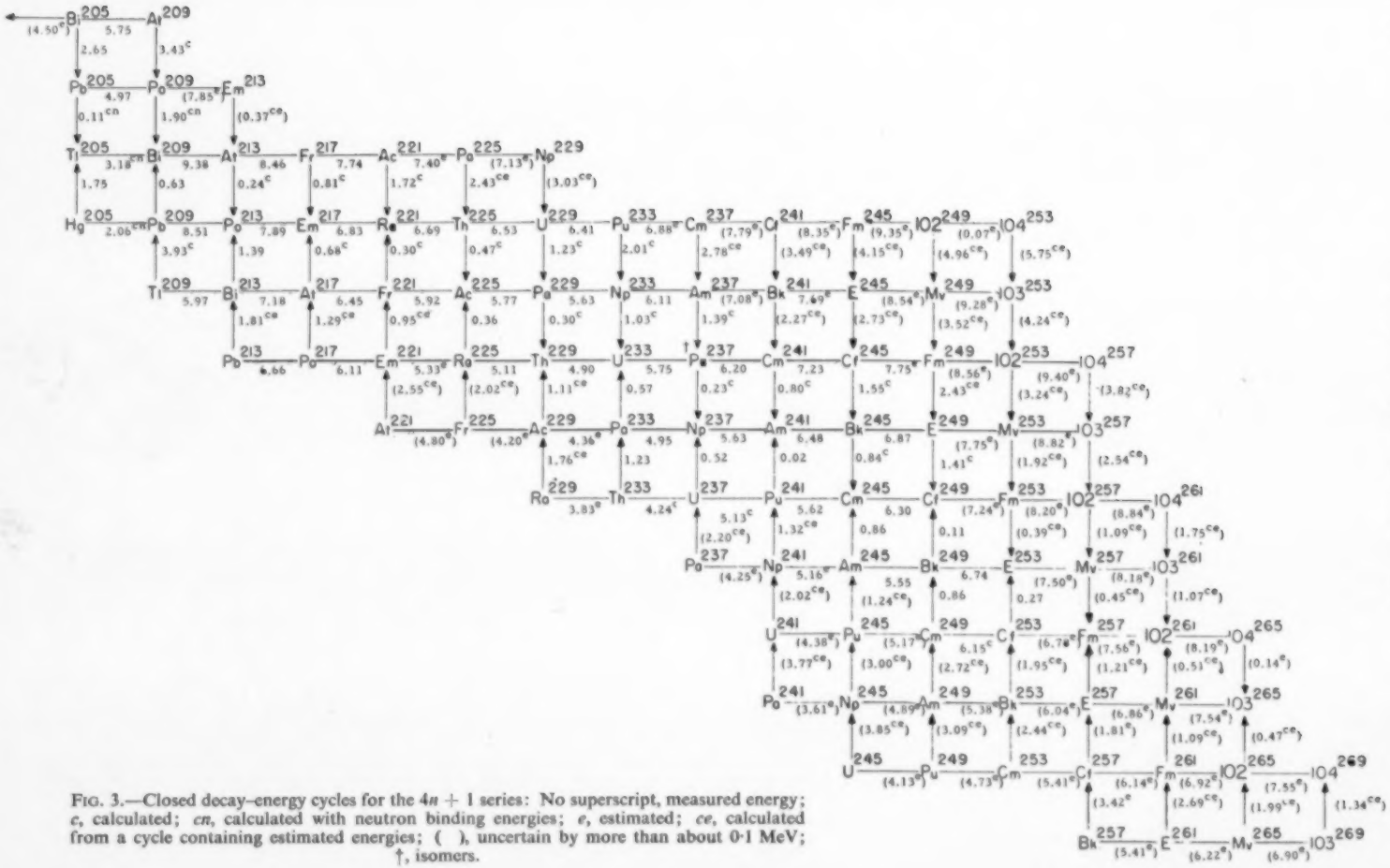

FIG. 3.—Closed decay–energy cycles for the $4n + 1$ series: No superscript, measured energy; *c*, calculated; *cn*, calculated with neutron binding energies; *e*, estimated; *ce*, calculated from a cycle containing estimated energies; ( ), uncertain by more than about 0·1 MeV; †, isomers.

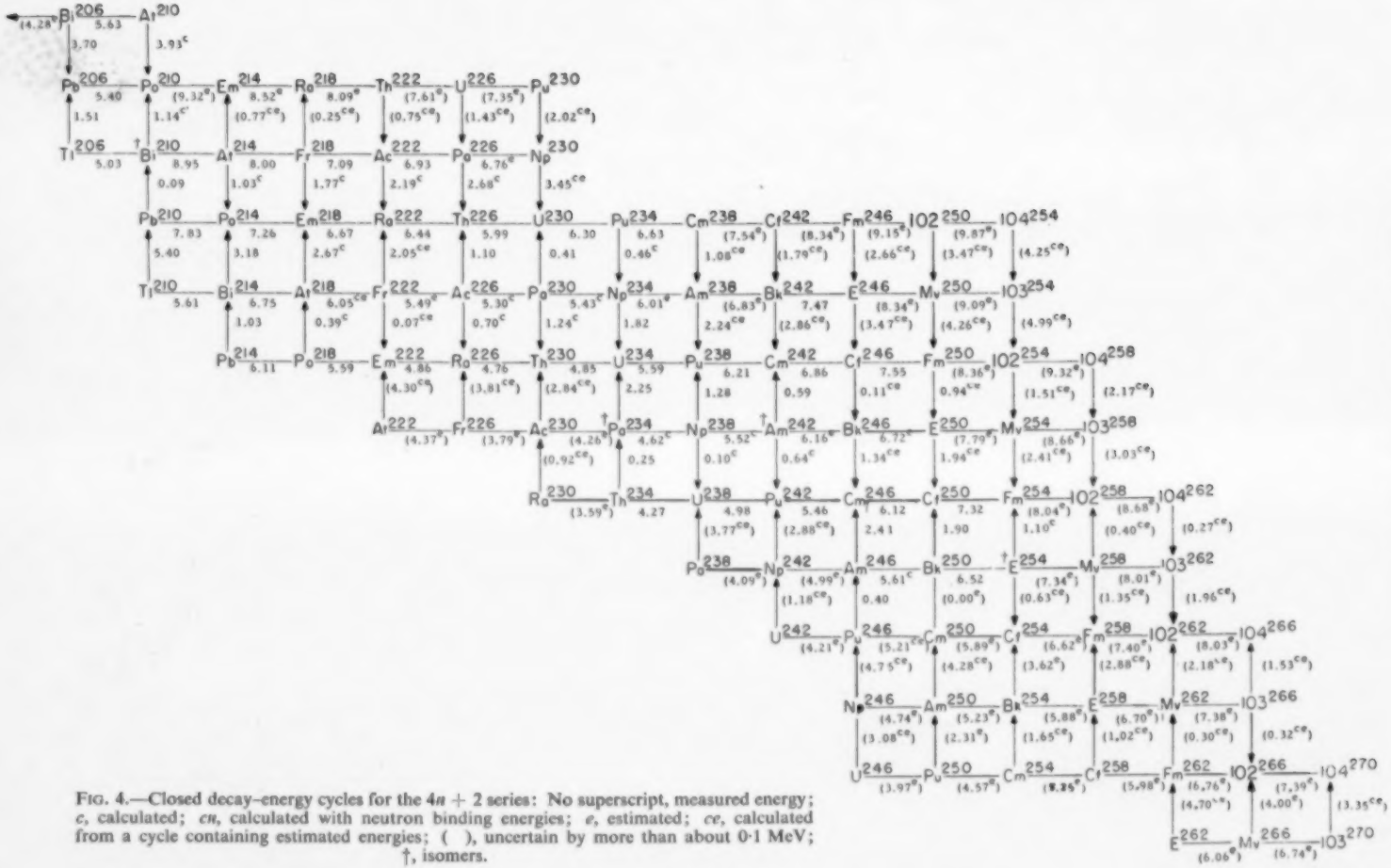

FIG. 4.—Closed decay–energy cycles for the $4n + 2$ series: No superscript, measured energy; *c*, calculated; *cn*, calculated with neutron binding energies; *e*, estimated; *ce*, calculated from a cycle containing estimated energies; ( ), uncertain by more than about 0·1 MeV; †, isomers.

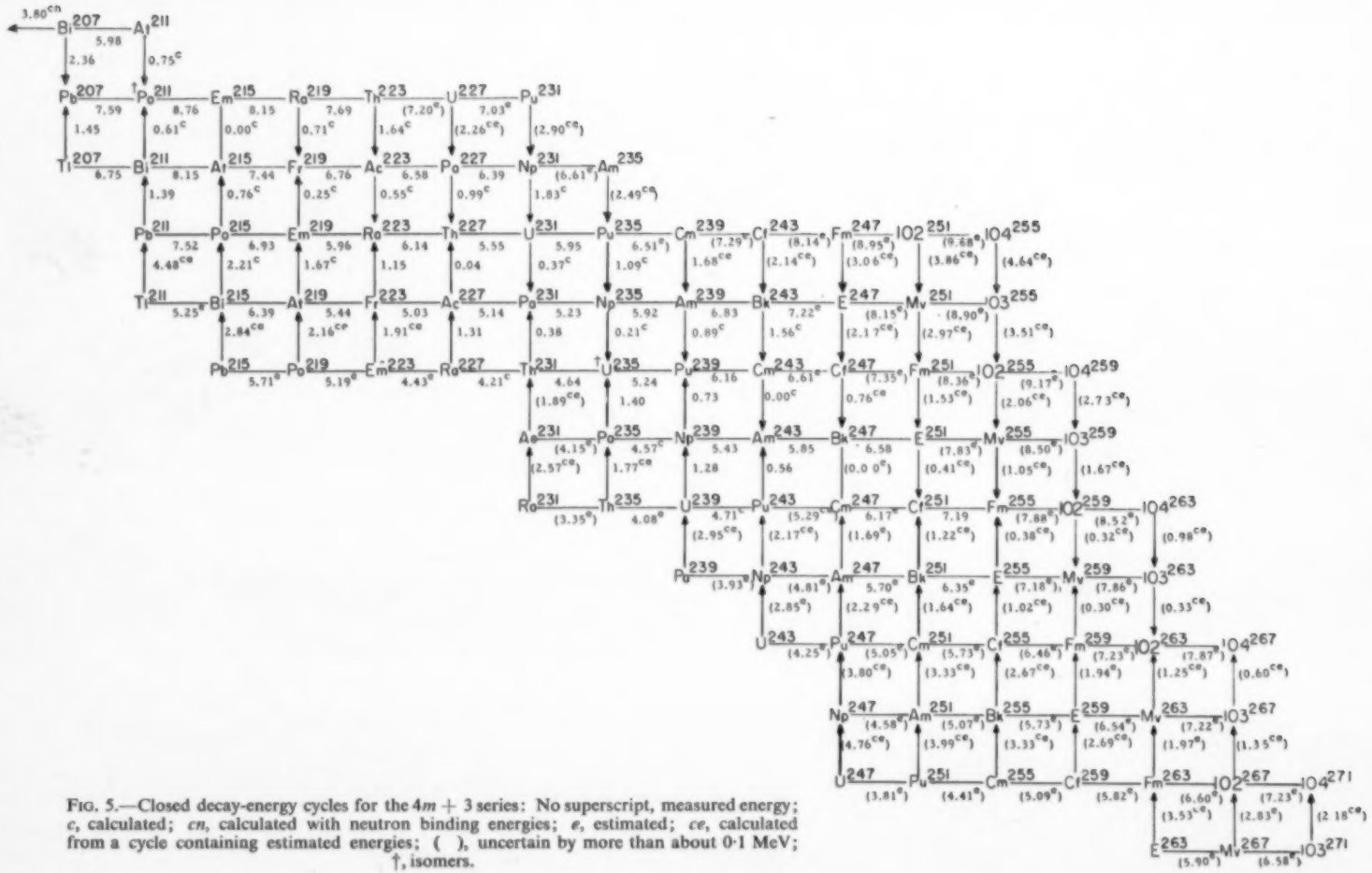

FIG. 5.—Closed decay-energy cycles for the $4m + 3$ series: No superscript, measured energy; *c*, calculated; *cn*, calculated with neutron binding energies; *e*, estimated; *ce*, calculated from a cycle containing estimated energies; ( ), uncertain by more than about 0·1 MeV; †, isomers.

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β-Decay. β-Decay energies have been plotted versus mass number in Figs. 7 and 8. Many values calculated from closed cycles containing known β-decay energies and measured, calculated, or estimated α-decay energies are included. Lines of constant atomic number Z have been drawn as well as lines of constant isotopic

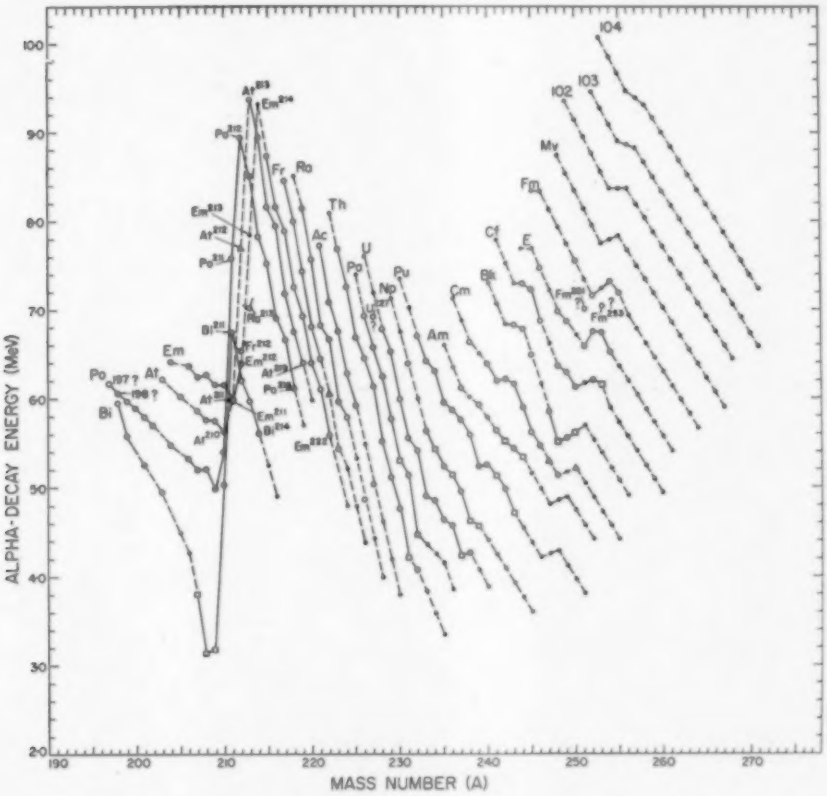

FIG. 6.—α-decay energies for the *trans*-lead nuclides as a function of mass number: ○, experimental energy; □, calculated; ●, estimated; △, calculated from a cycle containing estimated energies; ?, total decay energy in question.

number ($I = A - 2Z$). Some of the β-decay energies in Figs. 2–5 have been estimated by interpolating or extrapolating on these lines. It has not seemed feasible to extend this treatment below 126 neutrons.

MASSES AND BINDING ENERGIES

Although the closed cycles fix the relative energies and hence masses of all nuclides belonging to a given mass type, in order to determine the absolute masses it is necessary either to know the absolute mass of one nuclide of each type or to have some way of relating the four mass types. In the latter case it is sufficient to know the absolute mass of only one nuclide rather than four, and the four mass types can be related by neutron binding energies.

The most precise mass measurements are those obtained by mass spectrometry.

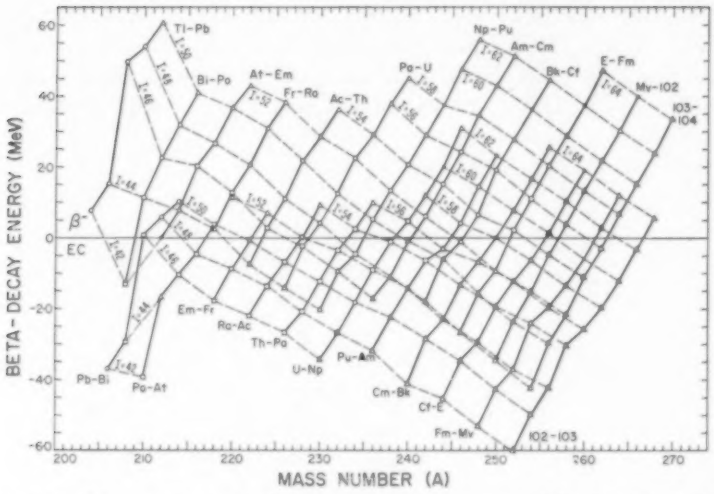

FIG. 7.—β-decay energies for the even-mass *trans*-mercury nuclides as a function of mass number: ○, experimental energy; □, calculated; ●, estimated; △, calculated from a cycle containing estimated energies.

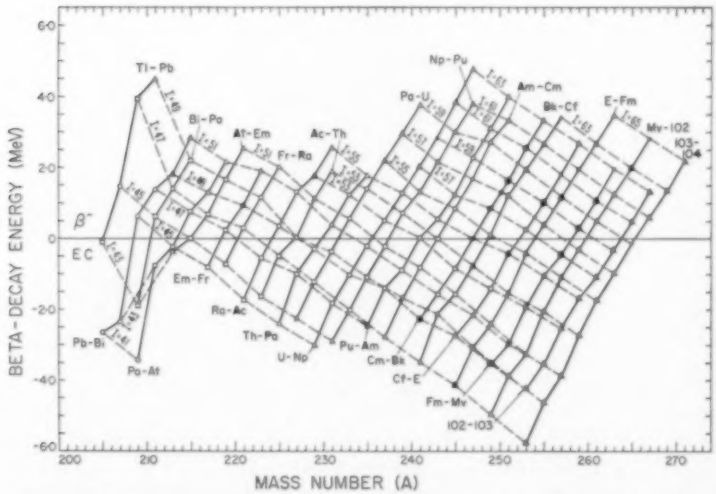

FIG. 8.—β-decay energies for the odd-mass *trans*-mercury nuclides as a function of mass number: ○, experimental energy; □, calculated; ●, estimated; △, calculated from a cycle containing estimated energies.

Even these, however, are rarely more precise than 0·001 mass units in the heavy region. Neutron binding energies, on the other hand, have been measured to a precision of 0·03 MeV, corresponding to 0·00003 mass units. Hence it seems advisable to adopt one measured mass as a standard and to calculate all the others relative to the mass of the standard nuclide.

The nuclide chosen for this purpose was ^{208}Pb, but use was made of the other measured masses in the heavy region in the following manner: by means of the

closed cycles and measured neutron binding energies we have obtained the mass difference between ^{208}Pb and other nuclides in the heavy region whose masses have been measured. The mass of ^{208}Pb was then calculated from each of these measurements and an average was taken. The measured masses and mass differences used for this calculation are listed in Table 1. The adopted value for the mass of ^{208}Pb and other auxiliary quantities used in calculating the masses and binding energies appear in Table 2.

TABLE 1.—MEASUREMENTS USED IN CALCULATING MASS OF ^{208}Pb

Nuclide	Measured mass	Ref.	Mass difference*	^{208}Pb mass calc.
^{208}Pb	208·0410 ± 0·0015	5	—	208·04100
^{209}Bi	209·0472 ± 0·0015	5	1·00415	208·04305
^{207}Pb	207·0429 ± 0·0016	6	1·00106	208·04396
^{208}Pb	208·0409 ± 0·0013	6	—	208·04090
^{234}U	234·1133 ± 0·0011	6	26·07246	208·04084
^{238}U	238·1234 ± 0·0010	6	30·08361	208·03980
^{232}Th	232·1093 ± 0·0010	7	24·06908	208·04022

* Difference between the mass of the nuclide in question and that of ^{208}Pb, as calculated from the closed cycles.

TABLE 2.—ADOPTED MASS OF ^{208}Pb AND AUXILIARY QUANTITIES

1. Masses:
   ^{208}Pb = 208·04140
   ^{4}He = 4·00387
   $^{1}_{0}$n = 1·00898[8]
   ^{1}H = 1·00814[8]

2. Neutron binding energies:
   $^{203-204}$Tl = 6·20 MeV
   $^{204-205}$Tl = 7·48
   $^{205-206}$Tl = 6·54
   $^{205-206}$Pb = 8·16
   $^{206-207}$Pb = 6·73
   $^{207-208}$Pb = 7·38
   $^{208-209}$Pb = 3·87
   $^{208-209}$Bi = 7·44

3. 1 atomic mass unit = 931·14 MeV[8]

Neutron and proton binding energies in the thallium–polonium region other than the measured ones were calculated with the aid of a set of closed cycles of a different kind, shown in Fig. 9. These binding energy cycles include nuclides of all mass types, so many different kinds of cycles can be closed on a diagram of this type, involving α- and β-decay energies and neutron and proton binding energies. These complicated cycles were used principally for calculating neutron and proton binding

[5] P. I. RICHARDS, E. E. HAYS and S. A. GOUDSMIT, *Phys. Rev.* **85**, 630 (1952).
[6] G. S. STANFORD, H. E. DUCKWORTH, B. G. HOGG and J. S. GEIGER, *Phys. Rev.* **85**, 1039 (1952).
[7] H. E. DUCKWORTH, *Nature, Lond.* **174**, 595 (1954).
[8] E. R. COHEN, J. W. M. DUMOND, T. W. LAYTON and J. S. ROLLET, *Rev. Mod. Phys.* **27**, 363 (1955).

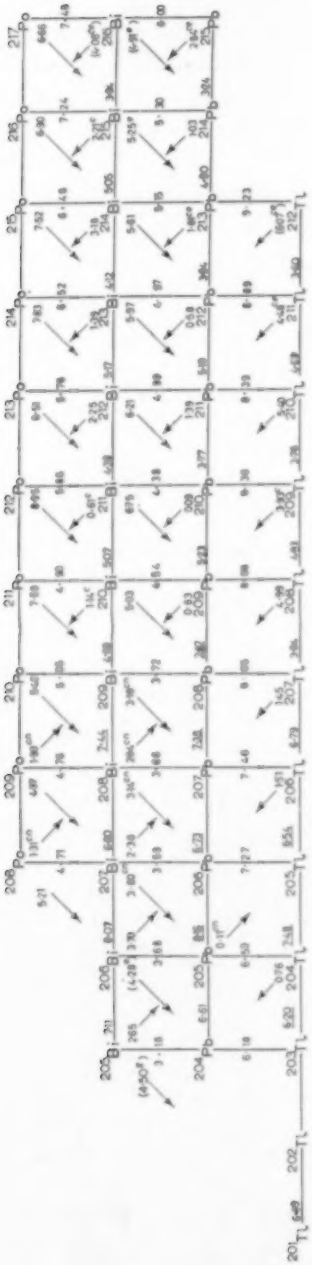

FIG. 9.—Binding energy cycles for the Tl–Po region. Neutron binding energies are on the horizontal lines; proton binding energies on the vertical lines; decay energies on the diagonal arrows. Decay energy notation: No superscript, measured energy; *c*, calculated; *cr*, calculated with neutron binding energies; *e*, estimated; *ce*, calculated from a cycle containing estimated energies; ( ), uncertain by more than about 0·1 MeV. Measured binding energies are underlined; all others are calculated.

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TABLE 3.—MASSES AND NEUTRON AND PROTON BINDING ENERGIES OF THE HEAVIEST ELEMENTS

Element	Mass	B_n (MeV)	B_p (MeV)
$_{81}$Tl	(201·03252)		
	(202·03410)	(6·89)	
	203·03492	(7·53)	
	204·03731	6·20 (meas)	
	205·03826	7·48 (meas)	
	206·04022	6·54 (meas)	
	207·04190	6·79	
	208·04676	3·84	
	209·05044	4·93	
	210·05539	3·76	
	211·05933	4·69	
	(212·06444)	(3·60)	
$_{82}$Pb	204·03650		6·18
	205·03838	6·61	6·59
	206·03860	8·16 (meas)	7·27
	207·04034	6·73 (meas)	7·46
	208·04140*	7·38 (meas)	8·05
	209·04622	3·87 (meas)	8·08
	210·04959	5·23	8·38
	211·05452	3·77	8·39
	212·05792	5·19	8·89
	213·06267	3·94	(9·23)
	214·06639	4·90	
	215·07189	3·24	
$_{83}$Bi	205·04122		3·18
	206·04257	7·11	3·68
	207·04288	8·07	3·59
	208·04456	6·80	3·66
	209·04555	7·44 (meas)	3·72
	210·04949	4·69	4·54
	211·05302	5·07	4·38
	212·05730	4·38	4·99
	213·06073	5·17	4·97
	214·06639	4·12	5·15
	215·06884	5·05	5·30
	(216·07359)	(3·94)	(6·00)
$_{84}$Po	208·04596		4·71
	209·04759	6·85	4·76
	210·04827	7·73	5·05
	211·05237	4·55	4·90
	212·05489	6·02	5·85

* Reference mass.

Table 3 (*continued*)

Element	Mass	B_n (MeV)	B_p (MeV)
$_{84}$Po (*contd.*)	213·05924	4·31	5·78
	214·06187	5·91	6·52
	215·06647	4·09	6·48
	216·06921	5·81	7·24
	217·07370	4·18	(7·48)
	218·07683	5·45	
	219·08189	3·65	
	(220·08509)	(5·39)	
$_{85}$At	209·05127		2·64
	210·05249	7·23	3·02
	211·05317	7·73	3·01
	(212·05669)	(5·09)	(3·56)
	213·05949	(5·75)	3·29
	214·06298	5·12	4·10
	215·06565	5·88	4·06
	216·06970	4·59	4·57
	217·07231	5·93	4·69
	218·07641	4·55	5·06
	219·07957	5·42	5·02
	(220·08388)	(4·35)	(5·73)
	(221·08687)	(5·58)	(5·92)
	(222·09132)	(4·22)	
$_{86}$Em	212·05669		4·31
	(213·05989)	(5·38)	(4·60)
	(214·06215)	(6·26)	(5·11)
	215·06565	(5·11)	5·09
	216·06752	6·62	5·84
	217·07148	4·58	5·83
	218·07354	6·54	6·44
	219·07778	4·42	6·30
	220·07995	6·34	7·23
	221·08413	4·47	(7·35)
	222·08670	5·97	(7·74)
	223·09134	4·05	(7·56)
	(224·09411)	(5·79)	
$_{87}$Fr	217·07245		2·99
	218·07544	5·58	3·99
	219·07751	6·44	3·88
	220·08089	5·22	4·69
	221·08311	6·29	4·64
	222·08678	4·95	5·12
	223·08929	6·03	5·17

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Table 3 (*continued*)

Element	Mass	B_n (MeV)	B_p (MeV)
$_{87}$Fr (*contd.*)	224·09335	4·58	5·71
	(225·09590)	(5·99)	(5·91)
	(226·09989)	(4·65)	
$_{88}$Ra	(218·07517)		5·05
	219·07828	(5·48)	4·94
	220·07952	7·20	5·71
	221·08279	5·32	5·81
	222·08458	6·70	6·22
	223·08806	5·13	6·39
	224·09003	6·52	6·89
	225·09373	4·92	7·23
	226·09580	6·44	(7·68)
	227·09997	4·48	(7·50)
	228·10222	6·27	
	229·10617	4·68	
	(230·10882)	(5·90)	
	(231·11316)	(4·33)	
$_{89}$Ac	221·08464		2·82
	222·08693	6·23	3·73
	223·08865	6·77	3·79
	224·09151	5·70	4·37
	225·09334	6·65	4·50
	226·09655	5·38	4·96
	227·09857	6·49	5·00
	228·10218	5·00	5·53
	229·10428	6·40	5·66
	(230·10783)	(5·06)	(6·04)
	(231·11040)	(5·98)	(6·11)
	(232·11435)	(4·68)	(6·47)
$_{90}$Th	(222·08773)		(4·70)
	223·09041	(5·88)	4·34
	224·09119	7·63	5·21
	225·09385	5·89	5·40
	226·09537	6·95	5·70
	227·09852	5·43	5·74
	228·09984	7·14	6·40
	229·10309	5·33	6·73
	230·10478	6·79	7·12
	231·10837	5·03	(7·08)
	232·11048	6·40	(7·51)
	233·11416	4·93	(7·76)
	234·11655	6·14	
	235·12063	4·57	
	(236·12343)	(5·75)	

Table 3 (*continued*)

Element	Mass	B_n (MeV)	B_p (MeV)
$_{91}$Pa	225·09646		2·68
	226·09825	6·70	3·49
	227·09959	7·12	3·65
	228·10209	6·03	4·26
	229·10341	7·13	4·25
	230·10611	5·85	4·77
	231·10796	6·65	4·62
	232·11085	5·67	5·27
	233·11284	6·51	5·38
	234·11628	5·16	5·61
	235·11873	6·09	5·55
	236·11237	4·97	5·96
	(237·12495)	(5·96)	(6·17)
	(238·12906)	(4·54)	
	(239·13205)	(5·58)	
	(240·13632)	(4·39)	
	(241·13961)	(5.30)	
$_{92}$U	(226·09978)		(4·49)
	(227·10201)	(6·29)	(4·07)
	228·10236	(8·04)	5·00
	229·10473	6·15	5·12
	230·10567	7·49	5·48
	231·10836	5·87	5·49
	232·10952	7·28	6·13
	233·11223	5·84	6·30
	234·11386	6·84	6·63
	235·11722	5·24	6·70
	236·11927	6·46	7·08
	237·12259	5·27	7·38
	238·12501	6·11	(7·53)
	239·12888	4·76	(7·74)
	240·13149	5·94	(8·11)
	(241·13556)	(4·57)	(8·29)
	(242·13859)	(5·54)	(8·53)
	(243·14321)	(4·07)	
	(244·14638)	(5·41)	
	(245·15149)	(3·60)	
	(246·15539)	(4·73)	
	(247·16084)	(3·30)	
$_{93}$Np	(229·10799)		(2·34)
	230·10938	(7·07)	3·26
	231·11032	7·49	3·25
	232·11241	6·42	3·81
	233·11333	7·50	4·03
	234·11582	6·05	4·24
	235·11745	6·85	4·24

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Table 3 (*continued*)

Element	Mass	B_n (MeV)	B_p (MeV)
$_{93}$Np (*contd.*)	236·12024	5·76	4·77
	237·12203	6·70	5·01
	238·12511	5·49	5·23
	239·12751	6·14	5·25
	240·13098	5·13	5·63
	241·13339	6·12	5·81
	(242·13732)	(4·70)	(5·94)
	(243·14014)	(5·74)	(6·13)
	(244·14424)	(4·55)	(6·62)
	(245·14736)	(5·46)	(6·67)
	(246·15208)	(3·96)	(7·03)
	(247·15572)	(4·98)	(7·27)
	(248·16084)	(3·60)	(7·58)
$_{94}$Pu	(230·11155)		(4·27)
	(231·11344)	(6·61)	(3·80)
	232·11343	(8·37)	4·69
	233·11549	6·44	4·71
	234·11631	7·60	4·81
	235·11862	6·22	4·97
	236·11969	7·37	5·50
	237·12228	5·95	5·69
	238·12374	7·00	5·99
	239·12672	5·59	6·08
	240·12878	6·45	6·40
	241·13197	5·39	6·66
	242·13423	6·26	6·80
	243·13781	5·03	(7·12)
	244·14024	6·10	(7·49)
	(245·14413)	(4·74)	(7·68)
	246·14698	(5·71)	(7·93)
	(247·15164)	(4·03)	(7·99)
	(248·15486)	(5·37)	(8·39)
	(249·15980)	(3·76)	(8·55)
	(250·16353)	(4·89)	
	(251·16880)	(3·46)	
$_{95}$Am	(235·12129)		(2·94)
	236·12311	(6·67)	3·40
	237·12377	7·75	3·78
	238·12615	6·15	3·98
	239·12768	6·94	3·91
	(240·13031)	(5·91)	(4·24)
	241·13195	(6·84)	4·63
	242·13492	5·60	4·84

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Table 3 (*continued*)

Element	Mass	B_n (MeV)	B_p (MeV)
$_{95}$Am (*contd.*)	243·13721	6·23	4·80
	244·14059	5·22	5·00
	245·14280	6·30	5·20
	246·14655	4·87	(5·33)
	(247·14918)	(5·92)	(5·53)
	(248·15332)	(4·51)	(6·02)
	(249·15648)	(5·42)	(6·07)
	(250·16105)	(4·11)	(6·42)
	(251·16452)	(5·14)	(6·66)
	(252·16946)	(3·76)	(6·97)
$_{96}$Cm	(236·12496)		(4·17)
	237·12675	(6·69)	4·19
	238·12731	7·85	4·29
	239·12948	6·34	4·47
	240·13041	7·50	5·04
	241·13281	6·13	(5·26)
	242·13428	6·99	5·41
	243·13721	5·64	5·44
	244·13898	6·72	5·94
	245·14188	5·66	6·38
	246·14397	6·42	6·50
	(247·14737)	(5·20)	(6·82)
	248·14964	(6·25)	(7·16)
	249·15356	4·71	(7·36)
	(250·15645)	(5·67)	(7·61)
	(251·16094)	(4·19)	(7·68)
	(252·16397)	(5·54)	(8·09)
	(253·16875)	(3·91)	(8·24)
	(254·17231)	(5·05)	
	(255·17741)	(3·62)	
	(256·18134)	(4·70)	
$_{97}$Bk	(240·13485)		(2·59)
	(241·13525)	(7·99)	(3·08)
	(242·13735)	(6·40)	(3·35)
	243·13889	(6·94)	3·29
	(244·14147)	(5·96)	(3·62)
	245·14278	(7·14)	4·04
	246·14540	5·92	4·30
	247·14737	6·54	4·41
	248·15038	5·56	(4·78)
	249·15264	6·26	4·79
	250·15645	4·81	4·89
	(251·15918)	(5·83)	(5·04)
	(252·16314)	(4·67)	(5·53)
	(253·16613)	(5·58)	(5·57)
	(254·17054)	(4·26)	(5·92)

Table 3 (*continued*)

Element	Mass	B_n (MeV)	B_p (MeV)
$_{97}$Bk (*contd.*)	(255·17383)	(5·30)	(6·16)
	(256·17861)	(3·92)	(6·47)
	(257·18211)	(5·10)	(6·87)
$_{98}$Cf	(241·13899)		(3·72)
	(242·13928)	(8·10)	(3·83)
	(243·14119)	(6·59)	(4·01)
	244·14211	(7·50)	4·58
	245·14445	6·19	(4·81)
	246·14552	7·36	5·03
	247·14818	5·89	4·99
	248·14968	6·97	5·43
	249·15252	5·72	(5·59)
	250·15441	6·60	5·93
	(251·15787)	(5·15)	(6·26)
	252·16018	(6·21)	(6·65)
	253·16404	4·77	(6·75)
	(254·16665)	(5·43)	(7·10)
	(255·17097)	(4·35)	(7·18)
	(256·17383)	(5·70)	(7·59)
	(257·17844)	(4·07)	(7·74)
	(258·18182)	(5·21)	(7·85)
	(259·18675)	(3·78)	
	(260·19051)	(4·86)	
$_{99}$E	(244·14699)		(2·18)
	(245·14738)	(8·00)	(2·68)
	246·14925	(6·62)	3·11
	247·15052	7·19	2·93
	(248·15284)	(6·20)	(3·25)
	249·15403	(7·25)	3·53
	250·15650	6·07	(3·88)
	251·15831	6·68	3·95
	252·16150	5·39	(4·20)
	253·16375	6·27	4·26
	254·16733	5·03	4·52
	(255·16987)	(6·00)	(4·58)
	(256·17368)	(4·82)	(5·06)
	(257·17649)	(5·74)	(5·10)
	(258·18073)	(4·42)	(5·45)
	(259·18386)	(5·45)	(5·68)
	(260·18846)	(4·08)	(5·99)
	(261·19179)	(5·26)	(6·39)
	(262·19717)	(3·36)	
	(263·20066)	(5·11)	

Table 3 (*continued*)

Element	Mass	B_n(MeV)	B_p(MeV)
	(245·15183)		(3·07)
$_{100}$Fm	(246·15211)	(8·11)	(3·18)
	(247·15380)	(6·79)	(3·34)
	(248·15451)	(7·70)	(3·86)
	249·15664	(6·38)	(4·04)
	250·15750	7·56	4·35
	(251·15995)	(6·09)	(4·36)
	252·16124	(7·16)	4·85
	(253·16417)	(5·64)	(5·10)
	254·16615	(6·52)	5·35
	(255·16946)	(5·28)	(5·59)
	256·17151	(6·46)	(6·06)
	(257·17519)	(4·93)	(6·17)
	(258·17763)	(6·09)	(6·52)
	(259·18178)	(4·51)	(6·60)
	(260·18447)	(5·86)	(7·02)
	(261·18890)	(4·23)	(7·17)
	(262·19212)	(5·37)	(7·28)
	(263·19687)	(3·94)	(7·85)
	(264·20046)	(5·02)	(7·77)
	(248·16025)		(1·58)
$_{101}$Mv	(249·16042)	(8·20)	(2·08)
	(250·16208)	(6·82)	(2·52)
	(251·16314)	(7·37)	(2·33)
	(252·16525)	(6·40)	(2·65)
	(253·16623)	(7·45)	(2·94)
	(254·16873)	(6·03)	(3·33)
	(255·17059)	(6·64)	(3·44)
	(256·17361)	(5·55)	(3·72)
	(257·17568)	(6·44)	(3·70)
	(258·17908)	(5·19)	(3·96)
	(259·18146)	(6·16)	(4·02)
	(260·18509)	(4·98)	(4·40)
	(261·18773)	(5·90)	(4·54)
	(262·19180)	(4·58)	(4·89)
	(263·19476)	(5·61)	(5·12)
	(264·19919)	(4·24)	(5·43)
	(265·20234)	(5·42)	(5·83)
	(266·20755)	(3·52)	
	(267·21087)	(5·27)	
	(249·16575)		(2·46)
102	(250·16581)	(8·31)	(2·57)
	(251·16729)	(6·98)	(2·73)
	(252·16779)	(7·89)	(3·25)
	(253·16971)	(6·58)	(3·43)
	(254·17036)	(7·76)	(3·74)

Table 3 (*continued*)

Element	Mass	B_n (MeV)	B_p (MeV)
102 (*contd.*)	(255·17280)	(6·09)	(3·79)
	(256·17410)	(7·16)	(4·32)
	(257·17685)	(5·80)	(4·57)
	(258·17865)	(6·68)	(4·81)
	(259·18180)	(5·44)	(5·05)
	(260·18367)	(6·62)	(5·52)
	(261·18718)	(5·09)	(5·63)
	(262·18945)	(6·25)	(5·98)
	(263·19342)	(4·68)	(6·07)
	(264·19594)	(6·01)	(6·48)
	(265·20021)	(4·39)	(6·63)
	(266·20325)	(5·53)	(6·74)
	(267·20783)	(4·09)	(7·31)
	(268·21125)	(5·18)	(7·23)
103	(252·17429)		(1·06)
	(253·17426)	(8·39)	(1·56)
	(254·17572)	(7·01)	(1·99)
	(255·17657)	(7·56)	(1·79)
	(256·17864)	(6·44)	(2·15)
	(257·17957)	(7·49)	(2·48)
	(258·18191)	(6·19)	(2·87)
	(259·18359)	(6·80)	(2·98)
	(260·18644)	(5·71)	(3·26)
	(261·18833)	(6·60)	(3·24)
	(262·19156)	(5·36)	(3·51)
	(263·19377)	(6·31)	(3·56)
	(264·19723)	(5·14)	(4·03)
	(265·19970)	(6·06)	(4·08)
	(266·20359)	(4·74)	(4·43)
	(267·20638)	(5·77)	(4·66)
	(268·21064)	(4·40)	(4·97)
	(269·21363)	(5·58)	(5·37)
	(270·21866)	(3·68)	
	(271·22181)	(5·43)	
104	(253·18044)		(1·86)
	(254·18028)	(8·51)	(1·98)
	(255·18156)	(7·17)	(2·14)
	(256·18185)	(8·09)	(2·67)
	(257·18368)	(6·66)	(2·89)
	(258·18424)	(7·84)	(3·24)
	(259·18652)	(6·24)	(3·28)
	(260·18763)	(7·33)	(3·82)
	(261·19021)	(5·96)	(4·07)
	(262·19185)	(6·84)	(4·31)

Table 3 (*continued*)

Element	Mass	B_n (MeV)	B_p (MeV)
104 (*contd.*)	(263·19482)	(5·60)	(4·54)
	(264·19652)	(6·78)	(5·02)
	(265·19985)	(5·26)	(5·14)
	(266·20195)	(6·41)	(5·49)
	(267·20574)	(4·83)	(5·58)
	(268·20810)	(6·17)	(5·99)
	(269·21219)	(4·55)	(6·14)
	(270·21506)	(5·69)	(6·25)
	(271·21947)	(4·26)	(6·82)

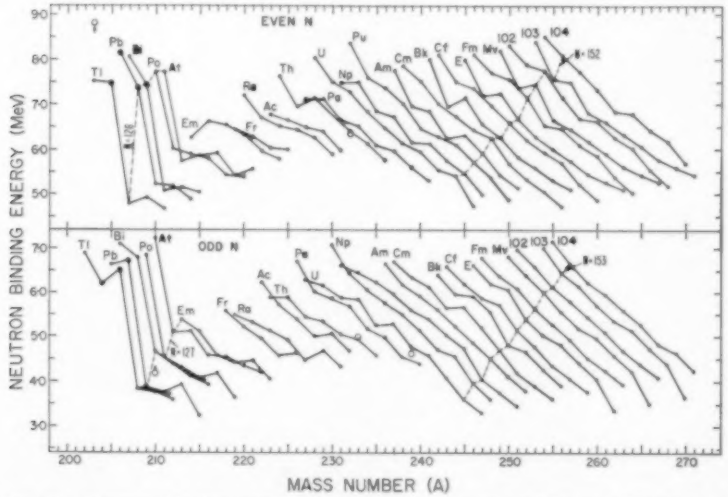

FIG. 10.—Neutron binding energies for the *trans*-mercury nuclides as a function of mass number: ●, measured energy used in calculations; ○, measured energy not used in calculation; ●, calculated energy. The neutron binding energy of ^{207}Tl should be plotted at 6·79 MeV.

energies in the region shown, although a few decay energies in this region were calculated with their aid.

The masses of most of the nuclides with $Z \geq 84$ were calculated on the IBM Type 650 Data Processing Machine of the University of California Radiation Laboratory, using data from the closed cycles. The neutron and proton binding energies of these nuclides were calculated on the same machine from mass differences. The neutron and proton binding energies of those few nuclides with $Z > 84$ whose masses were not calculated on the IBM 650 were calculated with the aid of closed cycles similar to those shown in Fig. 9.

Table 3 contains the masses and binding energies throughout the region covered by this paper. The binding energies listed are those of the last neutron or proton of the nuclide in question.

The neutron and proton binding energies are shown graphically in Figs. 10 and 11.

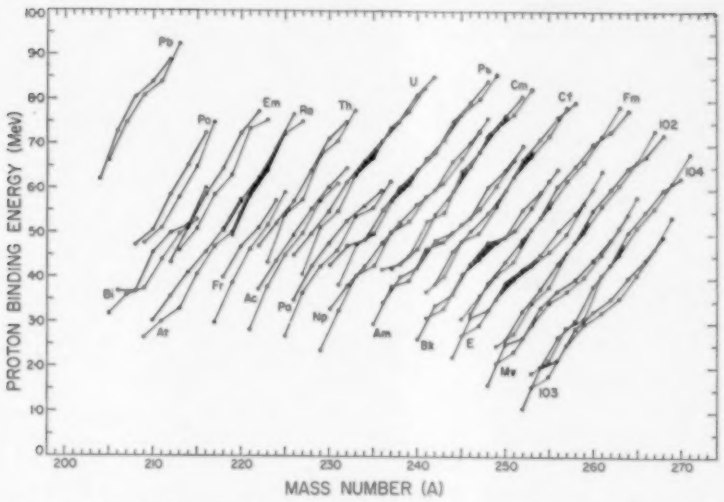

FIG. 11.—Calculated proton binding energies for the *trans*-mercury nuclides as a function of mass number.

HALF-LIFE SYSTEMATICS OF α- AND β-DECAY

In planning experiments to discover new isotopes, it is essential to make at least rough estimates of the half-lives involved. A knowledge of half-life systematics is also helpful in assigning the mass of a new isotope. It is largely for these practical reasons and for the purpose of making predictions in a later section that this section on half-life systematics is included.

A. *α-Half-life systematics*

α-Half-lives are quite well correlated through the use of quantum mechanical barrier penetration theory. However, for our purposes, it is easier and probably more accurate to use a semi-empirical treatment rather than to make use of the equations arising from the barrier penetration theory.

For this purpose, let us define a few terms. The effective α-decay energy Q_{eff} is given by:

$$Q_{\text{eff}} = Q_{\alpha} + \Delta E_{\text{sc}} \tag{1}$$

where ΔE_{sc} is the orbital electron screening correction and is given[9] by:

$$\Delta E_{\text{sc}} = 65{\cdot}3Z^{7/5} - 80Z^{2/5} \tag{2}$$

where ΔE_{sc} is in eV and Z is the atomic number of the decaying nucleus.

GALLAGHER and RASMUSSEN[9] show that if the logarithm of the partial ground-state α-half-life is plotted versus $Q_{\text{eff}}^{-1/2}$, a family of straight lines is obtained for even-even nuclides, one for each element, in accordance with the equation:

$$\log_{10}(t_{1/2})_{\alpha} = A_Z Q_{\text{eff}}^{-1/2} + B_Z \,. \tag{3}$$

Values of A_Z and B_Z for even Z are given in Table 4.

[9] C. J. GALLAGHER, JR. and J. O. RASMUSSEN, *J. Inorg. Nucl. Chem.* **3**, 333 (1957).

TABLE 4.—SEMI-EMPIRICAL CONSTANTS* FROM CORRELATION OF GROUND-STATE DECAY RATES OF EVEN-EVEN NUCLIDES

Z	A_Z	B_Z
84	129·35	−49·9229
86	137·46	−52·4597
88	139·17	−52·1476
90	144·19	−53·2644
92	147·49	−53·6565
94	146·23	−52·0899
96	152·44	−53·6825
98	152·86	−52·9506
100	156·38	−53·3742
102	159·05	−53·4945
104	161·72	−53·6148

* Constants for use in (3) with $(t_{1/2})_\alpha$ in seconds and Q_{eff} in MeV. Values for $Z > 98$ were obtained by extrapolation.

A least-squares fit to the values of A_Z and B_Z for $86 \leq Z \leq 98$ gives the following two equations:[10]

$$A_Z = 1{\cdot}33582Z + 22{\cdot}7969, \tag{4}$$

$$B_Z = -0{\cdot}060143Z - 47{\cdot}3599. \tag{5}$$

In Fig. 12 we have plotted the logarithm of the partial half-life for the ground-state α-transition versus Q_α for even-even α-emitters. The curves are calculated from equation (3), using the constants given in Table 4. The constants for elements 100, 102, and 104 were obtained from equations (4) and (5).

The partial α-half-lives of undiscovered nuclides can be estimated from Fig. 12 or equation (3). For nuclides with Z odd or $Z > 98$, the constants for use with equation (3) must be obtained from equations (4) and (5). For nuclides with unpaired nucleons, estimated hindrance factors must be used.

B. *β-half-life systematics*

β-half-lives are greatly dependent on the nuclear spectroscopic states of the parent and daughter nuclei. It is not the purpose of this paper to cover such detailed considerations. Paper I contains plots of the logarithm of the electron-capture or β-minus half-lives versus the logarithm of the decay energy for heavy nuclides. These can be used for making very rough estimates of β-half-lives.

SPONTANEOUS-FISSION SYSTEMATICS

The systematics of spontaneous-fission half-lives is of interest not only for predictive purposes, but also for more fundamental reasons. The dependence of spontaneous-fission half-lives on nuclear parameters such as Z, A, N, Z^2/A, etc., can be very helpful in elucidating the mechanism of fission and providing information about nuclear structure.

[10] C. J. GALLAGHER, JR., Private communication (1957).

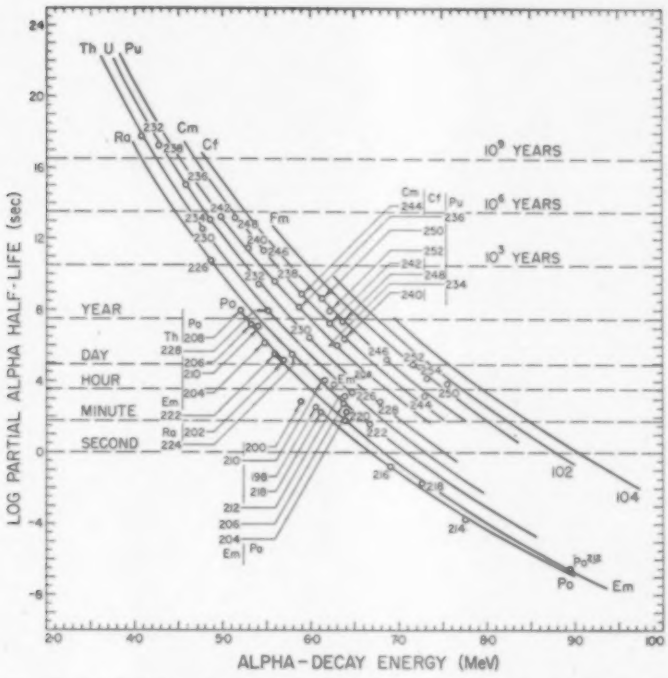

FIG. 12.—Partial half-lives for the ground state α-transitions of even-even nuclides as a function of their α-decay energies.

References to the older work on spontaneous-fission systematics can be found in Paper I.

SWIATECKI[11] found that if $\log (t_{\frac{1}{2}})_{SF}$ is plotted versus Z^2/A, the deviation from a straight line exhibits a correlation with the deviation of the mass from a smooth mass surface defined by a semi-empirical mass equation. He found, for even-even nuclides,

$$\log t_{\frac{1}{2}} = f(Z^2/A) - k\,\delta M \tag{6}$$

where $k \cong 5$, δM = experimental mass − mass from mass equation (in millimass units) and $f(Z^2/A)$ is a smooth function such that if $\log (t_{\frac{1}{2}})_{SF} + k\,\delta M$ is plotted versus Z^2/A, the resulting curves are almost straight lines for each of the three mass types, even-even, odd-A, and odd-odd.

SWIATECKI has also considered the energy difference between a smooth saddle-point energy surface (as a function of Z and N) and the actual ground-state masses.[12a,b] This difference gives the potential barrier for fission for any particular nuclide. The spontaneous-fission rate appears to increase by a factor of about 10^7 for each MeV decrease in the fission barrier. Thus it is possible that the spontaneous-fission rate of a nuclide of unknown mass can be used to determine the distance of its point on the saddle-point surface above its point on the ground-state surface, and hence can be used to determine its mass with high sensitivity if the

[11] W. J. SWIATECKI, *Phys. Rev.* **100**, 937 (1955).
[12a] W. J. SWIATECKI, *Phys. Rev.* **101**, 97 (1956); [b] W. J. SWIATECKI, Private communication (1957).

saddle-point surface is known or is assumed to be smooth. SWIATECKI has already pointed out[12b] that the mass of ^{256}Fm reported in this paper is somewhat lower than one would expect from the above considerations.

GHIORSO[13] has plotted the logarithm of the spontaneous-fission half-life for even-even nuclides versus neutron number and pointed out that the maximum half-life for a given element occurs at about $N = 152$ for the heaviest elements and that the logarithm of the half-life for $N > 152$ decreases approximately linearly with N for each element. It is interesting to note that these lines all have the same slope for $N > 152$ and that if the data are plotted versus mass number instead of neutron number all these lines coincide so that the spontaneous-fission half-life appears to depend only on the mass number. Fig. 13 is a plot of the logarithm of the spontaneous-fission half-life versus the mass number.

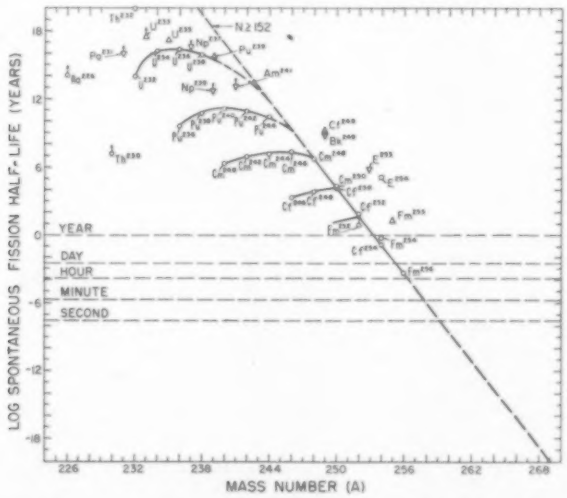

FIG. 13.—Partial spontaneous fission half-lives as a function of mass number: ○, even-even nuclide; △, even-odd nuclide; ▽, odd-even nuclide; □, odd-odd nuclide.

PREDICTIONS

From the systematics given in the earlier parts of this paper and from the β-half-life plots in Paper I, the decay energies and half-lives of a number of as yet undiscovered nuclides have been estimated. These are given in Table 5. The half-lives in this table for nuclides containing unpaired nucleons should be considered lower limits.

To the half-lives of the odd nucleon α-emitters in this table one should apply an "effective hindrance factor" defined as the ratio of overall α-half-life for the nuclide to that obtained from equation (3) for the same ground-state transition energy and atomic number. The values which should be used with Table 5 for the effective hindrance factor are about 5 for odd-even, 10 for even-odd, and 13 for odd-odd nuclides, found by taking a geometric mean of the known effective hindrance factors for each type.

[13] A. GHIORSO, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1955, Vol. 7, p. 15. United Nations (1956).

The mean spontaneous fission retardation factors to be used with Table 5 were found graphically from a plot similar to Fig. 13 and are 4×10^3 for odd-mass and 10^6 for odd-odd nuclides.

TABLE 5.—ESTIMATED NUCLEAR DECAY PROPERTIES OF UNDISCOVERED NUCLIDES (ALL HALF-LIVES ARE UNHINDERED VALUES)*

Nuclide	Q_α(MeV)	$t_{1/2}\alpha$	Q_{β^-}(MeV)	$t_{1/2}\beta^-$	Q_{EC}(MeV)	$t_{1/2}EC$	$t_{1/2}SF$
^{257}Fm	6·78	7 min	----β	stable	-------	----	1 min
^{259}Fm	6·62	300 days	----β	stable	-------	----	30 sec
^{253}Mv	7·95	10 min	—	—	3·73	10 min	1 yr
^{253}Mv	7·75	20 min	—	—	1·92	1 hr	2 yr
^{254}Mv	7·79	20 min	—	—	2·41	20 min	50 day
^{255}Mv	7·83	10 min	—	—	1·05	10 hr	2 day
^{257}Mv	7·50	2 hr	—	—	0·45	2 day	1 min
^{258}Mv	7·34	10 hr	0·40	2 day	1·35	2 hr	20 sec
^{252}102	8·76	1 sec	—	—	2·37	20 min	10 day
^{253}102	8·56	5 sec	—	—	3·24	10 min	20 day
^{254}102	8·36	20 sec	—	—	1·51	2 hr	50 day
^{255}102	8·36	20 sec	—	—	2·06	50 min	2 day
^{256}102	8·36	20 sec	—	—	0·45	2 day	5 hr
^{257}102	8·20	1 min	—	—	1·09	5 hr	1 min
^{258}102	8·04	5 min	----β	stable	-------	----	20 sec
^{255}103	8·90	1 sec	—	—	3·51	10 min	2 day
^{256}103	8·86	2 sec	—	—	4·23	5 min	5 hr
^{257}103	8·82	2 sec	—	—	2·54	20 min	1 min
^{258}103	8·66	5 sec	—	—	3·03	20 sec	20 sec
^{259}103	8·50	20 sec	—	—	1·67	2 hr	2 sec
^{260}103	8·34	1 min	—	—	2·58	20 min	0·1 sec
^{256}104	9·48	0·05 sec	—	—	2·99	20 min	5 hr
^{257}104	9·40	0·1 sec	—	—	3·82	10 min	1 min
^{258}104	9·32	0·2 sec	—	—	2·17	50 min	20 sec
^{259}104	9·17	0·5 sec	—	—	2·73	20 min	2 sec
^{260}104	9·00	1 sec	—	—	1·11	5 hr	0·1 sec
^{261}104	8·84	5 sec	—	—	1·75	1 hr	5×10^{-3} sec

* Average (and very approximate) hindrance and retardation factors for use with nuclides with unpaired nucleons are given in the text. Recent indications that the effect at 152 neutrons is diminishing with increasing Z suggest that the predicted half-lives for spontaneous fission for nuclides should be longer than listed here for $Z \geq 102$.

WHEELER,[14] basing his argument on the broad features of alpha decay theory and the Z^2/A correlation of spontaneous fission half-lives, predicts even-even nuclides with half-lives greater than 10^{-4} sec for nuclides with atomic number up to about 150 and mass number up to about 600. No such possibility is apparent in the systematics presented in this paper.

One source of the disagreement seems to lie in WHEELER's neglect of the very pronounced deviations which many nuclides show from the Z^2/A correlation. These deviations are of such a nature that heavier isotopes of an element have shorter spontaneous-fission half-lives rather than longer. This means that the isotopes of

[14] J. A. WHEELER, *Niels Bohr and the Development of Physics* (Edited by W. PAULI) p. 163. McGraw-Hill, New York (1955); F. G. WERNER and J. A. WHEELER, *Phys. Rev.* **109**, 126 (1958).

a given element with maximum spontaneous-fission half-life will have lower mass numbers than those considered by WHEELER.

In addition, WHEELER used a mass equation[15] which gives α-decay energies about 1 MeV lower than the experimental values in the region of fermium. The discrepancy is probably worse for higher values of Z. Thus α-decay half-lives will generally be shorter than those calculated by WHEELER. The α-half-lives will also be shorter because of the necessity, mentioned in the preceding paragraph, of considering lighter isotopes.

Since α-decay and spontaneous-fission are likely to be the only limiting modes of decay for these very heavy elements, we are forced to conclude that the heaviest nuclides obtainable with half-lives long enough to be studied in the laboratory will be much lighter than those predicted by WHEELER.

Acknowledgements—We deeply appreciate several helpful discussions with Drs. D. STROMINGER, J. M. HOLLANDER, F. ASARO, and F. S. STEPHENS, JR., regarding selection of data to be used in the cycles. We gratefully acknowledge stimulating discussions with Dr. W. J. SWIATECKI concerning spontaneous fission systematics and with Dr. C. J. GALLAGHER, JR., concerning α-half-life systematics. We wish to thank several members of the staff and graduate students at the University of California Radiation Laboratory for communicating their experimental results prior to publication.

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APPENDIX I. SOURCES OF DATA

Many of the data on alpha[16] and beta[17] disintegration energies were taken from recent review articles. Other data not appearing in these articles or in the Table of Isotopes[18] are listed in Table 6. Most of these data as well as data on spontaneous fission half-lives will appear in the new edition of the Table of Isotopes.[18]

TABLE 6.—NEW DECAY DATA

Nuclide	Mode of decay	Q (MeV)	$t_{1/2}$	Reference
^{208}Tl	β^-	4·99		19
^{210}Tl	β^-	5·40		20
^{214}Pb	β^-	1·03		21
^{205}Bi	EC	2·65		22
^{206}Bi	EC	3·7		23
^{207}Bi	EC	2·36		23
^{213}Bi	α	6·205		24
^{214}Bi	β^-	3·179		25

[15] N. METROPOLIS and G. REITWIESNER, *U.S. Atomic Energy Commission Document NP*-1980 (1950).
[16] I. PERLMAN and J. O. RASMUSSEN, *Alpha Radioactivity*, *UCRL*-3424, June 1956.
[17] R. M. KING, *Rev. Mod. Phys.* **26**, 327 (1954).
[18] J. M. HOLLANDER, I. PERLMAN and G. T. SEABORG, *Rev. Mod. Phys.* **25**, 469 (1953); see also D. STROMINGER, J. M. HOLLANDER and G. T. SEABORG, *Rev. Mod. Phys.* To be published (1958).
[19] F. DEMICHELIS, R. A. RICCI and G. TRIVERO, *Nuovo Cim.* (10) **3**, 377 (1956).
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Table 6 (*continued*)

Nuclide	Mode of decay	Q (MeV)	$t_{1/2}$	Reference
^{211}Po	α	7·586		26
^{208}Em	α		105 min	27
^{223}Fr	α	5·44		28
^{225}Ra	β^-	0·36		29
^{228}Ra	β^-	0·04		30
^{230}Ac	β^-	1·10		31
^{227}Ac	β^-	0·0455		32
^{231}Th	β^-	0·383		31, 33
^{225}Th	α	4·077		34
^{234}Th	β^- (to UX_2)	0·19		35
^{228}Pa	α	6·247		36
^{229}Pa	α	5·767		36
^{230}Pa	β^-	0·405	~90 days	37
^{231}Pa	α	5·138		38
^{233}Pa	β^-	0·568		39
^{234}Pa (UZ)	β^-	2·25		35
^{234}Pa (UX_2)	β^-	2·31		35
^{235}U	α	4·638		40
^{237}U	β^-	0·517		41
^{238}U	α	4·267		34
^{234}Np	EC	$\geq 1{\cdot}8_2$		42
^{235}Np	α	5·23		43
^{236}Np	β^-	0·518	(22 hr)	44
^{237}Np	α	4·950		45
^{238}Np	β^-	1·28		46, 47
^{239}Np	β^-	0·725		46, 48
^{240}Np	β^-	2·05	60 min	49

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Table 6 (*continued*)

Nuclide	Mode of decay	Q (MeV)	$t_{1/2}$	Reference
^{236}Pu	α		2·851 years	50
^{237}Pu	α	5·75	$3·6 \times 10^3$ years	51
^{243}Pu	β^-	0·56		52
^{246}Pu	β^-	0·400	10·85 days	53
^{239}Am	α	5·92		54
^{242}Am	β^-	0·585		55
^{242m}Am	β^-	0·620		55
^{244}Am	β^-	$\geq$1·5		56
^{245}Am	β^-	0·86		57
^{246}Am	β^-	2·41		58
^{241}Cm	α	6·20		31
^{246}Cm	α	5·462	6620 years	59
^{248}Cm	α	5·137	$4·7 \times 10^5$ years	59
^{249}Cm	β^-	0·86		60
^{245}Bk	β^-	0·65	23 days	61
^{249}Bk	β^-	0·11		62
	α	5·545		62
^{250}Bk	β^-	1·9	3·13 hr	63
^{245}Cf	α	6·30		62
^{253}Cf	β^-	0·27		10
^{246}E	α	7·47		64
^{250}Fm	α	7·55		65
^{252}Fm	α	7·16		66
	α		22·7 hr	67
^{256}Fm	α		~90 hr	68

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APPENDIX II. NEUTRON BINDING ENERGIES

The neutron binding energies adopted for the calculation of the masses were generally averages of measured values. The measured binding energies are given in Table 7, along with the corresponding adopted values.

TABLE 7.—MEASURED AND ADOPTED NEUTRON BINDING ENERGIES

Nuclides	Lower limit			Upper limit			Adopted
	B_n (MeV)	Reaction	Ref.	B_n (MeV)	Reaction	Ref.	
$^{202-203}$Tl				8·80 ± 0·20	(γ,n)	69	7·53*
$^{203-204}$Tl	6·54 ± 0·05	(n,γ)	70				6·20†
	6·52 ± 0·15	(n,γ)	70				
$^{204-205}$Tl				7·48 ± 0·15	(γ,n)	71	7·48‡
				7·55 ± 0·20	(γ,n)	69	
$^{205-206}$Tl	6·16 ± 0·15	(d,p)	70				6·54†
	6·20 ± 0·03	(n,γ)	72				
$^{205-206}$Pb				8·25 ± 0·10	(γ,n)	73	8·16‡
				8·10 ± 0·10	(d,t)	70	
				8·15 ± 0·05	(d,t)	74	
$^{206-207}$Pb	6·734 ± 0·01	(n,γ)	74	6·95 ± 0·10	(γ,n)	73	6·73‡
	6·71 ± 0·03	(d,p)	70	6·75 ± 0·20	(γ,n)	69	
				6·70 ± 0·05	(d,t)	70	
$^{207-208}$Pb	7·37 ± 0·03	(d,p)	73	7·44 ± 0·10	(γ,n)	73	
	7·380 ± 0·008	(n,γ)	74	7·30 ± 0·20	(γ,n)	74	7·38‡
				7·37 ± 0·05	(d,t)	70	
$^{208-209}$Pb	3·87 ± 0·05	(d,p)	70				3·87‡
$^{208-209}$Bi				7·45 ± 0·2	(γ,n)	75	7·44‡
				7·40 ± 0·20	(γ,n)	69	
				7·44 ± 0·05	(d,t)	70	
$^{209-210}$Bi	4·14 ± 0·03	(d,p)	70				4·69*
	4·170 ± 0·015	(n,γ)	74				
	4·17 ± 0·03	(d,p)	76				
$^{231-232}$Th				6·35 ± 0·04	(γ,n)	77	6·40*
$^{232-233}$Th	4·88 ± 0·20	(d,p)	70				4·93*
$^{237-238}$U				5·97 ± 0·10	(γ,n)	78	6·11*
				5·85 ± 0·15	(γ,n)	79	
$^{238-239}$U	4·63 ± 0·15	(d,p)	70				4·76*

* Calculated, this paper.
† See Appendix III.
‡ Measured value or average of measured values adopted.

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APPENDIX III. EXPLANATORY NOTES

In some cases, the choice of data for the cycles is not completely straightforward. In this section we will discuss some of the individual cycles, decay energies, and binding energies and will discuss the reasons for some of our choices.

Thallium neutron binding energies. Following FRITSCH,[80] we have interchanged the reported neutron binding energies of ^{204}Tl and ^{206}Tl. This interchange has three important results: the calculated electron capture decay energy of ^{205}Pb is much more reasonable, the neutron binding energies of the thallium and lead isotopes show a more systematic trend, and the calculated alpha decay energy of ^{209}Bi is much closer to the reported experimental results.[16]

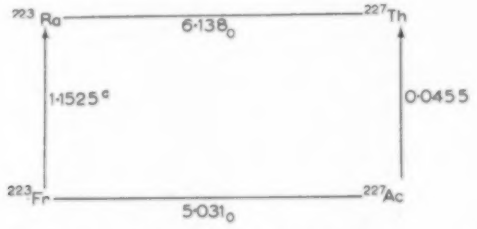

FIG. 14.—Closed cycle ^{227}Ac–^{223}Ra. Energies in MeV, same notation as Figs. 2–5.

^{212}At–^{212}Em. If the α-decay energy of ^{212}At is estimated to be exactly halfway between the values for ^{211}At and ^{213}At, the electron capture decay energy of ^{212}Em is calculated to be 0·01 MeV. Since there is no experimental evidence for the electron capture stability or instability of ^{212}Em, we estimated the energy difference between ^{212}Em and ^{212}At to be 0·00.

^{236}Np. The 22 hr isomer is included in the cycles. Since there are no data regarding the energy of transitions to or from the 5000 year isomer, there is no information as to which is the ground state.

^{240}U–^{240}Np. The β-decay energy of 0·47 MeV for ^{240}U is calculated from the known 0·36 MeV decay energy to the metastable state and 0·11 MeV excitation energy of that state.

^{241}Pu–^{237}Np *cycle.* The ^{241}Pu–^{237}Np cycle cannot be closed using the reported[16] α-decay energy of 5·121 MeV for ^{241}Pu. Since this is an even-odd nuclide and since ^{241}Am has been very thoroughly studied we must regard the α-decay energy of ^{241}Pu as the least well determined of the four energies in the cycle.

^{230}Pa. It has been reported that ^{230}Pa emits 0·4 MeV positrons,[37] but it is not possible to fit the resulting electron capture decay energy of 1·4 MeV into the cycles. The negatron decay energy of 0·405 MeV has been better determined,[37] so it has been used in the cycles.

^{254}E. The accuracy of the energy data on the decay of the isomers of ^{254}E is such that the decay energies of the two isomers are within experimental error of each other. We have included the α-decay energy of the 280 day isomer in the cycles.

^{247}Cm–^{247}Bk *and* ^{250}Cm–^{250}Bk. If the α-decay energies of ^{247}Cm and ^{250}Cm are estimated, the negatron decay energies of these isotopes are calculated to be very close to zero. Since no experimental evidence is available as to the β-stability of

[80] A. R. FRITSCH, Thesis, *UCRL*-3452 (1956).

these nuclides, we have estimated the negatron decay energy to be zero in each case and calculated the α-decay energies.

^{227}U, ^{251}Fm, *and* ^{253}Fm. The α-decay energies of ^{227}U, ^{251}Fm, and ^{253}Fm deviate from the systematic behaviour shown by the α-decay energies of the other isotopes of the same elements. Since these are even-odd nuclides, it is possible that the observed α-energies do not represent ground state transitions. Therefore the observed energies were not used in the cycles.

^{227}Ac–^{223}Ra *cycle*. The ^{227}Ac–^{223}Ra cycle, with energy values carried to four decimal places, is shown in Fig. 14. Note that the calculated negatron decay energy of ^{223}Fr agrees quite well with the measured value[17] of 1·15 MeV. Since we carry only two decimal places, we rounded off the negatron decay energy of ^{227}Ac to 0·04 instead of 0·05. By doing this, we were able to make maximum use of the available experimental data. (cf. Fig. 5).

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HALF-LIVES OF ^{204}Tl AND ^{134}Cs

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Abstract—Ionization measurements extending over a period of 6·3 years have yielded half-lives of 4·11 ± 0·13 years for ^{204}Tl and 2·26 ± 0·05 years for ^{134}Cs.

Thallium-204

A NUMBER of authors have reported a half-life of approximately 4 years for ^{204}Tl while others have reported a distinctly different value of about 2·5 years.

FAJANS and VOIGT[1] observed two deuteron-activated samples over a period of 300 days obtaining values of 4·0 ± 0·5 years and 3·1 ± 0·4 years with an average of 3·5 ± 0·5 years. HARBOTTLE[2] reported a half-life of 4·02 ± 0·12 years from a source which had been irradiated with reactor neutrons and counted at intervals for 2·9 years. A neutron-activated sample was followed for 3 years by HORROCKS and VOIGT[3] resulting in a half-life of 4·1 ± 0·1 years. TOBAILEM and ROBERTS[4] found a half-life of 4·26 ± 0·06 years after a 45 day observation of a reactor-produced sample. A mean value of 3·56 ± 0·05 year is quoted by MERRITT *et al.*[5] from 4·5 years of observations on two reactor-produced samples. LOCKETT and THOMAS[6] found after 3 years that their sample was deviating from a simple exponential decay. By analysing their data on the assumption that two periods were present they give values of 4·5 years ± 10% and 1·6 years ± 15%.

While studying the possible use of ^{204}Tl as a standard for assay work, REYNOLDS and BROOKSBANK[7] assayed a solution of ^{204}Tl then re-assayed it after 15 months and the results indicated a half-life of 2·7 years. A deuteron-activated thallium sample was observed by CHENG *et al.*[8] for 10 years. A half-life of 2·5 ± 0·03 years was obtained but no 4 years activity was found.

The activities of some long-period isotopes have been followed by the author since 1951. A sample of reactor-activated thallium in the form of a dry salt of thallium nitrate was obtained from the Oak Ridge National Laboratory through Tracerlab Inc. It was listed by ORNL at that time as a processed radioisotope, purified and analysed. Although no additional chemistry was done on the sample, a high degree of radioactive purity is indicated by the graph of the activity shown in Fig. 1. After 6·3 years no evidence of deviation from an exponential decay had been observed. The sample was mounted on a "Plexiglas" holder by spraying it with a thin coating of an acrylic polymer. Decay measurements were made with an ionization chamber attached to a

[1] K. FAJANS and A. F. VOIGT, *Phys. Rev.* **60**, 619 (1941).
[2] G. HARBOTTLE, *Phys. Rev.* **91**, 1234 (1953).
[3] D. L. HORROCKS and A. F. VOIGT, *Phys. Rev.* **95**, 1205 (1954).
[4] J. TOBAILEM and J. ROBERT, *J. Phys. Radium* **16**, 340 (1955).
[5] W. F. MERRITT, P. J. CAMPION and R. C. HAWKINS, *Canad. J. Phys.* **35**, 16 (1957).
[6] E. E. LOCKETT and R. H. THOMAS, *Nucleonics* **14** ,127 (1956).
[7] S. A. REYNOLDS and W. A. BROOKSBANK, JR., *Nucleonics* **11**, 46 (1953).
[8] L. T. CHENG, V. C. RIDOLFO, M. L. POOL and D. N. KUNDU, *Phys. Rev.* **98**, 231 A (1955).

Wulf unifilar electrometer. The chamber has a window of 0·001 in. aluminium and is filled with 1·1 atm of freon-12. The instrument was carefully calibrated with a radium standard before each set of readings. Each of the points in Fig. 1 represents

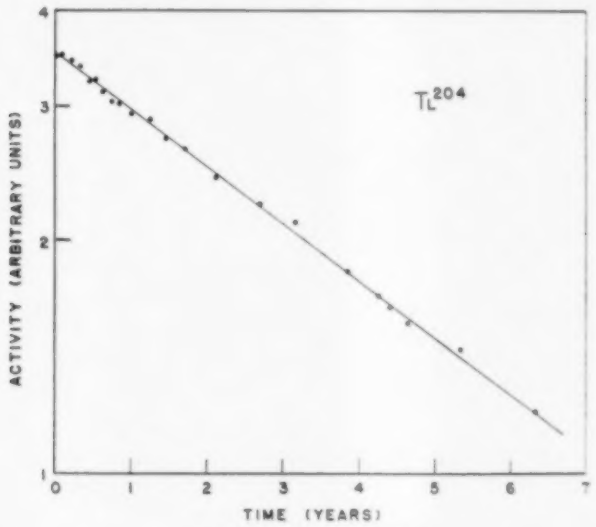

FIG. 1.—Decay of ^{204}Tl.

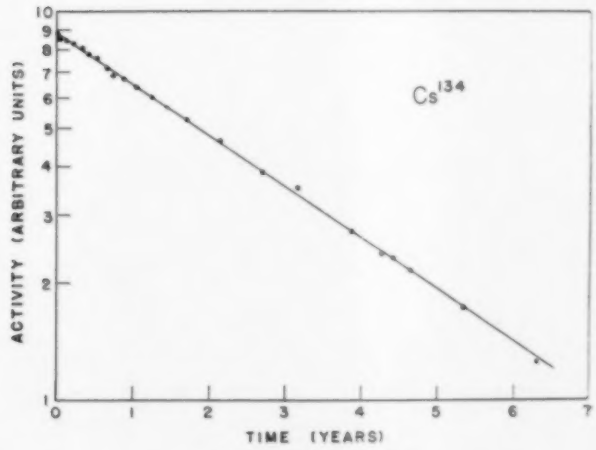

FIG. 2.—Decay of ^{134}Cs.

the weighted mean of at least 25 readings. An analysis of the best curve fit of the data yielded a half-life of 4·11 ± 0·13 years. This value agrees substantially with those of HARBOTTLE,[2] HORROCKS,[3] TOBAILEM[4] and LOCKETT.[6]

Caesium-134

KALBFELL and COOLEY[9] obtained a half-life of 1·66 ± 0·08 years from a sample produced by bombardment of caesium with cyclotron-produced neutrons or deuterons.

[9] D. C. KALBFELL and R. A. COOLEY, *Phys. Rev.* **58**, 91 (1940).

GLENDENIN[10] reported a half-life of 2·3 ± 0·3 years from counter observations for 13 months on a source activated by pile neutrons. A value of 2·19 ± 0·02 years in agreement with GLENDENIN was reported more recently by MERRITT *et al.*[5] Their observations were made with five sources which were irradiated in the Chalk River Reactor and recounted after a 5 year interval.

A source of neutron-activated ^{134}Cs was obtained by the author from Oak Ridge in 1951. It was listed as a processed isotope in the form of caesium chloride. The high degree of radioactive purity of this sample is shown by the graph in Fig. 2 which gives no indication of deviation from an exponential decay after observation through almost 3 half-lives. The caesium chloride was mounted and the activity observed in the same manner as that described above for thallium.

An analysis of the best curve fit of the data gave a half-life of 2·26 ± 0·05 years in good agreement with GLENDENIN[10] and MERRITT *et al.*[5]

[10] L. E. GLENDENIN, *Radiochemical Studies: The Fission Products* (Edited by C. D. CORYELL and N. SUGARMAN) NNES, Plutonium Project Record, Div. IV, Vol. 9, p. 1931. McGraw-Hill, New York (1951).

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A NEW METHOD FOR THE ABSOLUTE COUNTING OF ^{239}Np

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Abstract—A source of ^{243}Am with ^{239}Np in equilibrium has been standardized by α-counting the ^{243}Am and then used as a permanent standard source of ^{239}Np for counter calibration. The method has been checked by $4\pi\beta$-counting.

THE determination of the rate of production of ^{239}Pu by β-decay following neutron capture in ^{238}U is an important experimental step in the analysis of nuclear reactor performance. This determination can be achieved by the radioactive counting of ^{239}U or its decay products, ^{239}Np or ^{239}Pu. ^{239}U has a rather short half-life (23 min) and cannot be separated chemically from ^{238}U. ^{239}Pu has such a long half-life that its specific activity is too low for routine counting work. The 2·3 day β-emitter ^{239}Np is therefore generally used in these determinations. However, the absolute determination of ^{239}Np by β-counting presents some difficulties because the β-rays are of low energy and are accompanied by a large number of conversion electrons. For the usual routine end-window counter it is not possible to calculate the efficiency with adequate accuracy from the geometrical arrangement. Calibration by reference to some more elaborate counting method is therefore necessary. Two methods which have been used for this calibration are the windowless β-counter in 2π geometry and the α-counting of the ^{239}Pu daughter. The present report describes a new method based on the use of an α-standardized source of ^{243}Am with its daughter ^{239}Np in equilibrium. The decay chain of ^{243}Am to ^{239}Pu is shown in Fig. 1.[1] The decay rate of the ^{243}Am can be accurately determined by α-counting and the ^{239}Np β-decay rate is thus known with equal accuracy. If the source is covered with an absorber, thick enough to stop the ^{243}Am α-rays, it provides a permanent source of ^{239}Np β-rays and can be used for the calibration of any type of counter. The method has been tested by using it to calibrate an end-window Geiger counter (G.E.C. type 2B2) and comparing the result with a calibration of the same counter by reference to a ^{239}Np source which had been standardized by $4\pi\beta$-counting. The results are in good agreement.

RESULTS

Calibration of counter by the ^{243}Am *method*

The ^{243}Am source was supplied by the Chemistry Division at A.E.R.E., Harwell. It was produced by pile irradiation of ^{242}Pu followed by chemical separation of americium. Immediately after the separation, the source was β-counted in order to determine any β-emitting impurities before the ^{239}Np had grown in. The β-activity (attributed to ^{244}Cm impurity) observed in this initial count was less than 1 per cent of the equilibrium (^{239}Np) activity. The purity of the ^{243}Am was also checked by an

[1] J. M. HOLLANDER, I. PERLMAN and G. T. SEABORG, *Rev. Mod. Phys.* **25**, 469 (1952).

α-pulse-height analysis. Sources of about 10^4 dis/min and negligibly small solid content were prepared by evaporation of a few drops of the solution on polished disks of stainless steel. These disks were 1 in. in diameter and 0·018 in. thick. This type of mount was chosen because of its robustness as a standard source and because it is convenient for standardization by α-counting. This standardization was done by

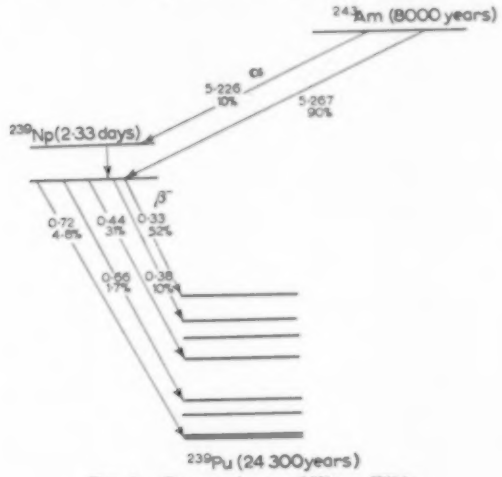

FIG. 1.—Decay scheme of ^{243}Am–^{239}Np.

comparison in an α-scintillation counter (A.E.R.E. type 1093) with a similarly mounted α-source which had been determined by counting in a proportional counter of known (low) geometry.

The end-window β-counter (2B2) has a 2 mg/cm² mica window rendered electrically conducting by coating with a layer of 0·1 mg/cm² of graphite. Sources can be mounted in reproducible geometry by the use of a "Perspex" shelf system in which the counter is firmly fixed. For the ^{243}Am calibration a 5 mg/cm² aluminium sheet was placed immediately below the counter window to stop the α-particles. The efficiency of the counter for ^{239}Np in these circumstances with a distance of 1 cm between the counter window and the top of the source disk was $0{\cdot}242 \pm 0{\cdot}003$.

The aluminium absorption curve for the ^{243}Am standard had a slightly steeper slope than the absorption curve obtained for a chemically pure source of ^{239}Np on the same type of mount. The difference corresponded to a component of half-thickness about 100 mg/cm² and intensity equal to 2 per cent of the total β-radiation as recorded through a 5 mg absorber. This could be explained by a 1·5 MeV β-impurity or by a 15 keV X-ray coming from the ^{243}Am decay. The first possibility seems to be eliminated by the original β-check and the X-ray intensity appears to be too low. However, making an allowance for this in the counter calibration, the final efficiency figure was $0{\cdot}237 \pm 0{\cdot}003$.

Calibration of counter by the $4\pi\beta$ method

The $4\pi\beta$-counter was a methane flow proportional counter (A.E.R.E. type 1364). Sources were mounted by evaporation from solution on thin plastic* foils of about

* A vinyl acetate/vinyl chloride co-polymer marketed by Bakelite Co. under the name of Vinylite VYNS.

20 mg/cm^2 which had been made conducting by the evaporation of an 8 μg/cm^2 thick layer of gold on one side.

For this calibration ^{239}Np was obtained by pile irradiation of natural uranium depleted in ^{235}U, thus reducing the amount of fission products. The neptunium was separated from most of the uranium by precipitation of the fluoride with neodymium carrier in the presence of hydrazine. The fluoride was converted to chloride, oxidised with nitric acid, dissolved in 11 M hydrochloric acid and the solution passed through a column of Deacidite F F. Plutonium was removed by washing the column with 11 M hydrochloric acid containing hydriodic acid. The neptunium was eluted from the column with 2 M hydrochloric acid. The solution thus obtained was evaporated with nitric acid to remove chloride and suitably diluted. Sources were made by weighing out portions of this solution and evaporating to dryness. The purity was checked by following the decay for twelve days. A half-life of 2·33 days was found. Sources were mounted on VYNS for $4\pi\beta$-counting and on stainless steel disks for comparison with the ^{243}Am counter calibration. Some additional sources were mounted on 0·0005 in. distrene sheet so that the "absolute" efficiency of the end-window counter, that is, without the backscatter and the aluminium absorption effects, could be determined. The solid content of the sources was negligibly small.

The steel disk sources were counted in the same positions below the 2B2 counter and with the same 5 mg absorber as in the ^{243}Am standardization. The distrene sources were counted in the same position but without the absorber. In calculating the counter efficiency some assumption has to be made about the efficiency of the $4\pi\beta$-counter for ^{239}Np. The efficiency of a similar counter for a β-ray of this energy has been shown by PATE and YAFFE[2] to be about 99 per cent. In the case of ^{239}Np, however, there is a large contribution from the conversion electrons and this tends to make up for the loss of true β-counts by absorption in the source or film. The number of such conversion electrons is 1·02 per β-disintegration[3,4] and on this basis the $4\pi\beta$ efficiency has been assumed to be 100 per cent. The resulting efficiency for the steel disk source through the absorber was 0·233 $\pm$ 0·002, and for the distrene source with no absorber 0·279 $\pm$ 0·003.

The ratio of these two efficiencies is 1·20, the steel disk result being smaller because the increase due to back-scattering is more than compensated by the absorption in 5 mg of aluminium.

CONCLUSION

The difference between the counter efficiencies determined by the ^{243}Am and the $4\pi\beta$ methods is 2 per cent, which is within the experimental errors. The mean of the two results gives a 2B2 counter efficiency for a steel disk ^{239}Np source at 1 cm with a 5 mg aluminium absorber interposed of 0·235 $\pm$ 0·002. Using this result with the distrene/steel disk efficiency ratio of 1·20, the best value for the "absolute" efficiency (no backscatter, no additional absorber) at 1 cm is 0·282 $\pm$ 0·003. This compares with a geometrical efficiency of 0·195 determined by a standard ^{32}P source at 1 cm from the same counter. The ^{239}Np "absolute" efficiency at 1 cm is thus determined from the geometrical efficiency by applying a correction factor of 1·45 to allow for the net effect of the conversion electrons and the air and window absorption. However,

[2] B. D. PATE and L. YAFFE, *Canad. J. Chem.* **33**, 929 (1955).
[3] J. M. HOLLANDER, W. G. SMITH and J. W. MIHELICH, *Phys. Rev.* **102**, 740 (1956).
[4] D. ENGELKEMEIR and L. B. MAGNUSSON, *Phys. Rev.* **99**, 135 (1955).

rather than use these factors, it is more straightforward in routine work to mount the ^{239}Np samples on steel disks and compare them directly with the ^{243}Am standard through a 5 mg absorber. This emphasizes the advantage of the method in providing a permanent standard source of ^{239}Np, thus eliminating the need for constant calibration with a 4π counter.

The method is versatile and the comparison can be done if necessary with a γ-counter using the prominent ^{239}Np peaks at 227 and 278 keV. Considerably stronger sources are required to obtain the same precision as in the β-comparison but the method is useful for thick sources or liquids.

Acknowledgements—Acknowledgement is due to Dr. F. MORGAN who suggested the ^{243}Am method of standardization and to Dr. J. MILSTED who supplied the ^{243}Am source.

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RADIOCHEMICAL STUDIES OF THE INTERACTION OF COPPER WITH 980 MeV PROTONS

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Abstract—The distribution of product nuclides from the bombardment of copper with 980 MeV protons has been investigated by radiochemical methods. The results are compared with results of similar work using protons of other energies.

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WHEN this investigation was undertaken, other workers had already examined spallation reactions in copper with protons of up to 100 MeV energy,[1] with 340 MeV protons[2] and with 2·2 BeV protons.[3] The variation of the relative yield of different spallation products between 340 MeV and 2·2 BeV suggested that experiments with protons of 980 MeV, which are available from the Birmingham proton synchrotron, would be useful. Later, VINOGRADOV *et al.*,[4] using 680 MeV protons and COLEMAN and TEWES,[5] using 90 and 190 MeV protons, studied similar spallation reactions. In all these experiments, the final nuclei resulting from spallation processes were examined radiochemically. This method enables the atomic and mass numbers of the radioactive nuclei to be determined unequivocally as well as giving a measure of the probability of formation.

The reactions occurring in copper under bombardment are typical of those which will occur in other elements of approximately the same weight. Copper has the advantage of availability in fine foils of high purity, it is easily handled in target preparations and lends itself well to chemical manipulations.

BATZEL *et al.*, using 340 MeV protons, found that the reaction products from copper covered a range from the region of the target nucleus to a region removed from the target nucleus by as many as forty or more nucleons. About 80 per cent of the total yield was concentrated in the elements copper, nickel and cobalt. VINOGRADOV *et al.*, using 680 MeV protons, found that elements near the target nucleus accounted for about 60 per cent of the total yield and that in general the yields of the products far removed from the target had increased substantially. The results of FRIEDLANDER *et al.*, using 2·2 BeV protons from the Brookhaven Cosmotron show that yields near the target nucleus are considerably decreased at this energy while the loss of fifteen or more nucleons is much more probable.

Among the elements studied were copper, iron, chromium and vanadium, representing products near to the target in mass, and also chlorine, potassium and fluorine

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(1) J. W. MEADOWS, *Phys. Rev.* **91**, 885 (1953).
(2) R. E. BATZEL, J. MILLER and G. T. SEABORG, *Phys. Rev.* **84**, 671 (1951).
(3) G. FRIEDLANDER, J. M. MILLER, R. L. WOLFGANG, J. HUDIS, and E. BAKER, *Phys. Rev.* **94**, 727 (1954).
(4) A. P. VINOGRADOV, I. P. ALIMARIN, V. I. BARONOV, A. K. LAVRUKHINA, T. V. BARANOVA and F. I. PAULOTSKAYA, *Conference of the Academy of Sciences U.S.S.R. on Peaceful Uses of Atomic Energy* (1955). (A.E.C. Report Tr-2435. Pt. 2 1956).
(5) G. H. COLEMAN and H. A. TEWES, *Phys. Rev.* **99**, 288 (1955).

representing the lighter products. The production cross-sections of their isotopes relative to ^{61}Cu were measured.

EXPERIMENTAL PROCEDURES

(a) *Irradiation techniques and targets*

Spectrometrically pure copper foils of thickness 0·001 in. were used as targets. The target stack consisted in general of six or seven foils of copper and one foil of polythene having a surface density of 5 mg/cm². The polythene foil was included as a monitor in order to obtain an absolute production cross-section for ^{61}Cu (Section 4). The foils were clamped in a clip holder and then shaped so that each foil presented an identical area to the beam. The bombardments took place in the internal circulating beam of the proton synchrotron using a moving target, which was projected into the proton beam at the end of the acceleration cycle, and withdrawn again after 1 sec. Bombardment times varied between 10 and 40 min, depending on the isotopes being investigated, at a pulse rate of one per 10 sec, the average beam intensity per pulse being 5×10^9 protons/cm². After bombardment, the foil stack was cut while the foils were still in the clip, thus obtaining foils of identical size, 1 cm × 0·5 cm area.

(b) *Chemical procedures*

Standard radiochemical procedures were adopted, using 10 mg amounts of carriers. Chemical yields were obtained by weighing the active samples after counting, except in the case of iron, where colorimetric estimation was used.

The elements were precipitated as follows, after initial solution of the target in nitric acid and the necessary separation and purification procedures:—

Copper	as copper thiocyanate.
Iron	as ferric hydroxide after ether extraction from 7 N HCl.
Chromium	as barium chromate, after removal of copper and manganese, and separation, by ether extraction, of peroxychromic acid.
Vanadium	as lead vanadate after removal of chromium by the above method.
Chlorine	as silver chloride.
Potassium	as potassium perchlorate.
Fluorine	as calcium fluoride.

In all cases, the final precipitates were mounted from an acetone slurry on either copper trays or aluminium trays. The amount of carrier used, generally between 5 and 10 mg, was such as to give a source thickness of about 5 mg/cm², care being taken to obtain a uniform layer.

(c) *Counting techniques*

Activities were determined using suitably shielded standard GM4 Geiger counters. Before any chemical separations were carried out, each target foil was counted for 1 min under a given counter. It was first proved by experiment and later assumed for each run that within statistics there was no difference in the activity between the front and back foil of the target stack. Thus the 1 min count provided an inter-calibration between the counters used for the separated fractions. The polythene foil was counted for a half-life or so under the counter to be used for the chemically separated copper and then the decay followed to background level on another counter.

The chemically separated fractions were mounted on aluminium counting trays of suitable thickness to provide saturation backscattering for most β-energies involved. In cases where aluminium could not be used because the chemical compounds reacted strongly with it and prevented an accurate determination of the chemical yield, thick copper trays (0·75 g/cm²) were employed.

The presence of a particular isotope in a given chemical fraction was indicated by its characteristic half-life. Only the isotopes that decayed by β-emission were identified. All measured activities, extrapolated back to the midtime of bombardment, were corrected for counter background, deadtime losses and chemical yield. Further corrections (Section 3) were applied for the effects of scattering and absorption of the decay electrons and also for branching-ratios.

Corrections

BURTT[6] has shown that for beta particles with $E_{max} > 0{\cdot}58$ MeV, saturation backscattering is independent of E_{max} for a given element as backscatterer. No corrections were made for this effect wherever aluminium counting trays were used to mount the chemically separated fractions, since most of the β-energies involved were above the lower limit. The counting trays used provided saturation backscattering to at least $E_{max} = 1{\cdot}6$ MeV. Since these trays were also used to hold the polythene monitor foils, the effect of backscattering was ignored in the calculation of the ^{61}Cu cross-section relative to that of ^{11}C produced in the carbon of the polythene.

Thick copper trays were employed to mount the potassium fraction. The correction required to bring these observed counting rates to those which would have been observed if aluminium backing had been used was determined experimentally. Weightless sources of ^{32}P and ^{204}Tl were counted alternately on the copper and aluminium trays. The backscattering corrections so found were in agreement with those of BURTT as shown in Table 1.

TABLE 1.—BACKSCATTERING CORRECTION—COPPER TO ALUMINIUM

Isotope	Energy (MeV)	Ratio $\frac{\text{counts/min on Cu}}{\text{counts/min on Al}}$
This work		
^{32}P	1·701	1·18 ± 0·01
^{204}Tl	0·765	1·18 ± 0·01
BURTT[6]		
^{32}P	1·701	1·17
^{131}I	0·608	1·16

A substantial amount of carrier was used to separate each fraction from the bombarded copper, so that corrections were necessary for the effects of self-absorption and self-scattering. Since the counting arrangements were similar and since saturation backscattering from aluminium was used, corrections were obtained from the published data of STEVENSON and NERVICK.[7] For molecular weights different from the two used by STEVENSON and NERVICK extrapolation was necessary for certain β-energies not included by these workers.

The self-absorption correction for the 5 mg/cm^2 polythene monitor foils was obtained from the work of HINTZ and RAMSEY.[8] Since the mean atomic number of the polythene (5·3) was so much less than that of the lightest salt used by STEVENSON and NERVICK (NaCl—14·7) a more accurate value for the correction was felt to be indicated by the former work.

Corrections to the observed counting rates for absorption of the β-particles in the air and counter window were made for β-particles with $E_{max} < 1{\cdot}5$ MeV. The half-thickness values used were those given by WHITEHOUSE and PUTMAN.[9] Calculations showed that correction for β-energies greater than 1·5 MeV were negligible.

In general the relative error due to counting errors and non-uniformity of sources for each ratio of cross-sections amounted to about 15 per cent. Errors involved in correcting for self-absorption

[6] B. P. BURTT, *Nucleonics* **5**, 28 (1949).
[7] P. C. STEVENSON and W. E. NERVICK, *Nucleonics* **10**, 3 (1952).
[8] F. HINTZ and N. RAMSEY, *Phys. Rev.* **88**, 19 (1952).
[9] W. J. WHITEHOUSE and J. L. PUTMAN, *Radioactive Isotopes*. Oxford University Press (1953).

and self-scattering were probably of the order of 5 per cent while those for counter window thickness were approximately 2 per cent. In the case of potassium fractions, another correction for back-scattering was necessary, introducing a further error of 5 per cent. Thus it is felt that the results for each isotope relative to the rest are good to within about 17 per cent.

The results obtained for the chlorine fraction are less reliable than other results given. A magnetic analyser was used to separate the positrons and electrons. It was impossible to calculate the corrections necessary for the effects of absorption and scattering, and hence the absolute efficiency of the analyser was unknown. However, the (^{34}Cl + ^{38}Cl) fraction was counted on an end window GM4 counter, and the magnetic analyser only used to obtain the ^{34}Cl/^{38}Cl ratio, so that the error in the case of the more abundant ^{34}Cl will be somewhat larger than that quoted above, while the ^{38}Cl yield, compared with ^{61}Cu may be in error by a factor 2.

It should be noted that, as in earlier work[10] no correction has been applied for differential backscatter of positrons and electrons.

Since the counters used are sensitive to electrons, but hardly at all to γ-rays, it was necessary to consider in each case the number of electrons emitted per nuclear transition by each radioactive isotope counted. This ratio was taken to be 100 per cent for each of the isotopes identified, which are listed in Table 2, with the exception of the following:—

^{64}Cu β^- decay in 58 per cent of the transitions
^{61}Cu β^+ decay in 72 per cent of the transitions
^{52}Fe β^+ decay in 59 per cent of the transitions[11]
^{48}V β^+ decay in 58 per cent of the transitions
^{18}F β^+ decay in 97 per cent of the transitions

The ^{52}Fe was counted in equilibrium with its 21 min ^{52}Mn daughter, and allowance was made for this in calculating the true yield of ^{52}Fe.

RESULTS

(a) *Absolute cross-section for* ^{61}Cu

A direct comparison of the corrected counting rate of the ^{61}Cu component in the copper fraction with the corrected ^{11}C counting rate in polythene, assuming a ^{11}C cross-section of 28·4 mbarns,[12] gives an absolute cross-section for the production of ^{61}Cu from natural copper of 10·2 $\pm$ 1·4 mbarns.

(b) *Relative cross-section for other products*

Table 2 lists the cross-sections for formation of the products found, relative to ^{61}Cu taken as 1·00. Each figure represents the mean of at least three, and in some cases six, separate determinations. For completeness, results at other energies obtained in other laboratories are quoted in Table 3, figures for cross-sections being quoted relative to ^{61}Cu taken as 1·00. This method of presentation has been adopted to avoid a lengthy discussion of the most reasonable cross-section to adopt for any given monitor reaction.

CONCLUSIONS

It is possible to calculate to within about 30 per cent the yield of the long-lived and stable isotopes produced in the spallation of medium weight elements. The

[10] G. A. CHACKETT, K. F. CHACKETT, P. REASBECK, J. L. SYMONDS and J. WARREN, *Proc. Phys. Soc.* A **69**, 43 (1956).
[11] E. ARBMAN and N. SVARTHOLM, *Arkiv. Fysik.* **10**, 1 (1956).
[12] This figure has been obtained by a consideration of the following work on the ^{12}C(p,pn)^{11}C reaction. W. E. BURCHAM, J. L. SYMONDS and J. D. YOUNG, *Proc. Phys. Soc.* A **58**, 1001 (1955); J. B. CUMMING, G. FRIEDLANDER and C. SCHWARTZ, *Bull. Amer. Phys. Soc.* **1**, 225 (1956); A. H. ROSENFELD, R. A. SWANSON and S. D. WARSHAW, *Phys. Rev.* **103**, 413 (1956).

TABLE 2.—CROSS-SECTIONS RELATIVE TO ^{61}Cu OF ISOTOPES PRODUCED IN COPPER BY 980 MeV PROTONS

Element	Isotope	Half-life	No. of determinations involved	Cross-section relative to ^{61}Cu	Error (%)
Copper	^{64}Cu	12·8 hr	6	2·02	±17
	^{62}Cu	9·8 min	6	2·21	±17
	^{61}Cu	3·33 hr		1·0	
	^{60}Cu	23·4 min	6	0·40	±17
Iron	^{59}Fe	9 min	5	0·15	±20
	^{52}Fe	8 hr	5	0·043	±20
Chromium	^{49}Cr	41·8 min	5	0·30	±15
Vanadium	^{48}V	16·2 days	4	2·54	±20
	^{47}V	32 min	4	0·25	±20
Potassium	^{44}K	22 min	5	0·034	±17
	^{43}K	22 hr	5	0·27	±17
	^{42}K	12·5 hr	5	0·23	±17
	^{38}K	7·7 min	5	0·04	±17
Chlorine	^{38}Cl	55·5 min	3	0·06	
	^{36}Cl	37·3 min	3	0·08	
	^{34}Cl	33·2 min	3	0·37	
Fluorine	^{18}F	112 min	3	0·19	±22

TABLE 3.—COMPARISON OF RESULTS AT VARIOUS PROTON ENERGIES (CROSS-SECTIONS ARE RELATIVE TO THAT OF ^{61}Cu)*

Isotope	340 MeV BATZEL *et al.*	680 MeV VINOGRADOV *et al.*	980 MeV This paper	2·2 BeV FRIEDLANDER *et al.*
$^{64}Cu/^{61}Cu$	0·98	0·361	2·0	1·1
^{62}Cu	2·1	1·31	2·2	2·6
^{61}Cu	1·0	1·0	1·0	1·0
^{60}Cu	—	0·052	0·40	0·28
^{59}Fe	0·073	0·128	0·15	0·2
^{52}Fe	0·008	0·0056	0·043	0·028
^{49}Cr	0·041	0·097	0·30	0·34
^{48}V	0·032	0·055	2·54	1·48
^{47}V	—	0·0805	0·25	0·42
^{44}K	—	0·000524	0·034	—
^{43}K	—	0·00411	0·27	0·2
^{42}K	—	0·00941	0·23	0·57
^{38}K	—	0·000575	0·04	—
^{38}Cl	0·0004	0·000368	0·06	0·062
^{36}Cl	0·0025	0·00162	0·08	0·10
^{34}Cl	0·0003	0·000694	0·37	0·14
^{18}F	—	—	0·18	0·15

*MARKOWITZ[13] finds the following cross-section ratios from the bombardment of natural Cu with 1 BeV protons:— ^{64}Cu—1·3, ^{62}Cu—2·5, ^{60}Cu—0·3.

[13] S. S. MARKOWITZ, Ph. D. Thesis, Princeton (1957).

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method most suitable for this has been outlined by RUDSTAM.[14] It is based on the assumption that for bombarding particles of sufficiently high energy the formation cross-sections of the various product nuclei are independent of the individual properties of the nuclei and will vary in a regular manner with the distance from the bombarded nucleus. In this way a complete picture of the interaction of a high energy particle with a medium weight element is obtained.

It is evident in the light of work at lower energies that the isotopes with the greatest yields are those which have mass numbers nearest that of the target nucleus and, as other workers have found, the yields of nuclides further removed from the target become smaller. However a comparison of the present work at 980 MeV with the results obtained at 340 and 680 MeV indicates that the yields of nuclides with mass numbers far removed from that of the target are considerably greater at 980 MeV that at the lower energies. The results reported here are in general of the same order of magnitude as those found by FRIEDLANDER *et al.*[3] at 2·2 BeV.

It appears, in this work, as in similar studies, that the nuclides with the largest neutron deficiencies or neutron excesses are formed in the lowest yields and the yields for any given atomic number appear to rise for nuclides nearest the region of stability. The stable nuclides are probably formed with the highest yields. Similarly it seems that the nuclides formed with a mass near that of the target nucleus are all neutron deficient while for smaller masses, neutron excess isotopes are formed in large yield. The high yield of these neutron-excess isotopes is perhaps due in part to the fact that it requires less energy for the excited parent to emit α-particles or larger fragments than a series of neutrons and protons.

The results of (1) BATZEL (340 MeV), (2) VINOGRADOV (680 MeV), (3) this paper (980 MeV) and (4) FRIEDLANDER (2·2 BeV) have been represented as a contour map on plots of N and Z of the products (Fig. 1). Each contour represents a factor of ten in yield on an arbitrary scale. Circles represent nuclides whose yield have been measured, or those where the yield can be obtained by interpolation from neighbouring nuclides. The dashed line approximates the centre of the stable isotopes of each element, and the stars represent the target nuclei.

It would appear that the most probable reactions at 340 MeV are those in which protons and neutrons are ejected in approximately the ratio of two neutrons to each proton, since the major proportion of each contour line lies on the neutron deficient side of the stability line. It can also be seen that products only a few nucleons lighter than the target nuclei are present in great preponderance, with rapid fall-off in the amount of those products which require larger numbers of nucleons to be removed from the target nuclei.

In the diagram for 680 MeV, it is still apparent that more neutrons than protons are being ejected, but now the yield of products many nucleons lighter than the target material is greatly enhanced.

In the diagram for 980 MeV, the ratio of neutrons to protons ejected appears to be much closer to one neutron for each proton, as is also the case for the distribution of products at 2·2 BeV. In these latter two diagrams, the large increase in the proportion of products far removed from the target nuclei is shown quite clearly. Thus, the production of ^{44}Sc, formed by the ejection of 20 nucleons, appears to be almost as high as the production of ^{61}Cu, only two nucleons removed from a target nucleus.

[14] S. G. RUDSTAM, *Phil. Mag.* **46**, 344 (1955).

In general, the observed distribution of products at each energy would fit in well with the nuclear disruption mechanisms suggested by WOLFGANG *et al.*[15] namely, spallation, fission and fragmentation processes. The fragmentation referred to is taken to be a process which is fast compared to the lifetime of a compound nucleus.

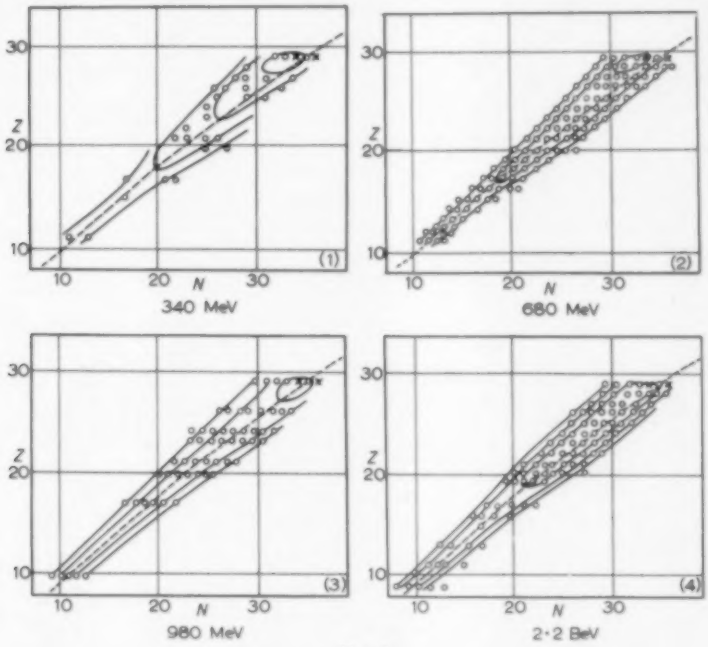

FIG. 1.

The nucleon cascade, and the production, scattering and reabsorption of mesons results on the deposition of large amounts of available energy in relatively small zones of the nucleus,* causing cohering masses of nucleons to be removed from the nucleus as separate fragments. The marked difference for the product distributions shown between the 340 MeV and the 680 MeV diagrams is probably due to some extent to the onset of pion production at about 400 MeV incident particle energy.

Multiple pion production and nuclear fragmentation processes will also probably contribute towards the rapid increase of lighter products ($20 < A < 40$) indicated at the higher energies, as opposed to the production of other nuclides by spallation or fission processes.

It can be concluded that in the formation of various product nuclides from the interaction of copper with 980 MeV protons the fraction of the total yield of products

*If the radius constant is taken to be $1{\cdot}3 \times 10^{-13}$ cm, the radius of the ^{64}Cu nucleus is $5{\cdot}2 \times 10^{-13}$ cm. The total π^+–p cross-section at 150 MeV, for example, is taken to be 140 mbarns.[16] This corresponds to a mean free path of $6{\cdot}4 \times 10^{-14}$ cm for pions in nuclear matter, and would indicate that the probability of escape of the pion from the nucleus in which it is created is very low, so that the probability for transfer of an average of 20–30 MeV per collision to neighbouring nucleons through scattering processes is high. This, in conjunction with meson absorption by pairs of nucleons, presumably results in a fast local heating, breaking nuclear bonds and causing the fragmentation.

[15] R. WOLFGANG, E. W. BAKER, A. A. CARETTO, J. B. CUMMING, G. FRIEDLANDER and J. HUDIS, *Phys. Rev.* **103**, 394 (1956).

[16] J. S. LINDENBAUM and L. C. L. YUAN, *Phys. Rev.* **100**, 306 (1955).

made by the knock-on process is still considerable, though relatively less important here than at lower energies. Reactions involving the transfer of very high excitation energies to the struck nucleus, resulting in the emission of a large number of particles, are still somewhat less probable than reactions in which only a small number of particles are emitted. However, these complex reactions are much more likely at 980 MeV than at 340 MeV, indicating that greater excitation energy is given on average to the struck nucleus during the initial interaction, allowing the evaporation of larger numbers of particles in the second stage.

FRIEDLANDER *et al.*, who obtained similar results at 2·2 BeV, suggest that greater excitation energy is given to the struck nucleus by the production and reabsorption of mesons within the nucleus. In this connexion it is interesting to note that the production cross-section for ^{48}V is of the same order of magnitude as those for copper isotopes. It appears that about 15 to 17 MeV excitation energy is lost per nucleon evaporated from an excited target nucleus consisting of many nucleons.[17,18] On this basis, the energy removed from a Cu target nucleus in forming a ^{48}V nucleus (representing the loss of 15 to 17 nucleons) would be between about 225 and 289 MeV. The π-mesons created in nucleon–nucleon collisions have been shown to have energy spectra which are quite sharply peaked at low energies (at about 100 MeV) with a large proportion of the mesons having energies between 80 and 150 MeV.[19] In addition, there appears to be a resonance at a pion energy of about 140 MeV in the cross-section for absorption of pions by nucleons.[20] Thus it would appear that both production and reabsorption of pions with energies in the range about 90 to 150 MeV would be favoured. Taking 139 MeV as the rest energy of the pion, this would indicate that in this range of pion energies, about 230 to 290 MeV excitation energy should be made available to the Cu nucleus by a large proportion of pion interactions. This would appear to offer an explanation of the high yield of ^{48}V observed (along with a correspondingly high yield of other nuclides in the region of ^{48}V). If calculated values of production cross-sections, obtained for example by the method of RUDSTAM,[14] are compared with the experimental values at 2·2 BeV and 980 MeV, there appears to be a broad maximum in the mass-yield curve in about the region $45 < A < 51$. However, a more extensive radiochemical survey would be needed to establish whether such a mechanism would serve to account for the favoured yield of products so many nucleons removed from the target nucleus.

Acknowledgements—The authors are greatly indebted to Dr. and Mrs. K. F. CHACKETT for their help in this work. It is a pleasure also to thank Dr. J. L. SYMONDS and the operating staff of the Birmingham proton synchrotron for their co-operation.

[17] K. J. LE COUTEUR, *Proc. Phys. Soc.* A **63**, 259 (1950).
[18] E. BELMONT and J. M. MILLER, *Phys. Rev.* **95**, 1554 (1954).
[19] L. C. L. YUAN and J. S. LINDENBAUM, *Phys. Rev.* **93**, 1431 (1954).
[20] M. G. MESHCHERYAKOV and B. S. NEGANOV, *Dokl. Akad. Nauk SSSR* **100**, 677 (1955).

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AN EMPIRICAL METHOD FOR ESTIMATING THE ELECTRON AFFINITIES OF ATOMS*

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Abstract—A new empirical method is developed for estimating values of the electron affinities of atoms. The method differs from other empirical calculations of electron affinities in that it depends essentially on the extrapolation of *one* known affinity in each period to give the affinities of the other elements in that period.

Electron affinity values are estimated for the following elements: beryllium, boron, carbon, nitrogen, oxygen, magnesium, aluminium, silicon, phosphorous, sulphur, zinc, gallium, germanium, arsenic, selenium, cadmium, indium, and tellurium. In the few cases where experimental results are available the estimated affinities are in excellent agreement with the experimental affinities.

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THE considerable difficulties involved in direct determinations of electron affinities of atoms have prompted the development of several empirical and semi-empirical methods for their estimation.[1–5] These methods may be summarized as follows: (1) Quadratic extrapolation of isoelectronic ionization potentials.[1] (2) Quadratic extrapolation of isoelectronic *first* excited term values.[2] (This gives an estimate of the electron affinity if it is assumed that the first excited term of a negative ion lies only slightly below or slightly above the limit of the continuum.) (3) Extrapolation of the mean binding energy per p electron in the successive states of ionization of an atom.[3] (4) Use of the BACHER and GOUDSMIT relations between the energy of an atom or ion and the values for various terms in its successive states of ionization.[4] (5) Calculation of the energies of the members of an isoelectronic sequence by a quantum mechanical variational procedure; followed by a quadratic extrapolation of the difference between the observed and calculated energies, for the neutral atom and positive ions in the sequence, to obtain a correction for the calculated energy of the negative ion after WU[4] and MOISEIWITSCH.[5]

All of these methods make use of a relation between term values of the members of an *iso*electronic sequence or between term values of an atom in its successive states of ionization. In each case the relation used is *known* to hold for the neutral atom and positive ions; it is *assumed* to hold also for the corresponding negative ion, so that the electron affinity (i.e., the ionization potential of the negative ion) may be calculated from the observed term values for the neutral atom and positive ions. Because of the

* This work was supported in part by the AEC.

(1) G. GLOCKLER, *Phys. Rev.* **46**, 111 (1934); D. R. BATES, *Proc. Roy. Irish Acad.* **51** A, 151 (1947); H. O. PRITCHARD, *Chem. Rev.* **52**, 529 (1953); S. GELTMAN, *J. Chem. Phys.* **25**, 782 (1956); Y. P. VARSHNI and S. N. SRIVASTAVA, *Z. physik. Chem.* **206**, 221 (1957).
(2) D. R. BATES and B. L. MOISEIWITSCH, *Proc. phys. Soc.* (Lond.) **68** A, 540 (1955).
(3) H. HELLMANN and M. MAMOTENKO, *Acta physicochim. URSS* **7**, 127 (1937); J. L. MARGRAVE, *J. Chem. Phys.* **22**, 636, 1937 (1954); H. O. PRITCHARD and H. A. SKINNER, *J. Chem. Phys.* **22**, 1936 (1954).
(4) R. F. BACHER and S. GOUDSMIT, *Phys. Rev.* **46**, 948 (1934); T-Y WU, *Phil. Mag.* **22**, 837 (1936).
(5) B. L. MOISEIWITSCH, *Proc. Phys. Soc.* A **67**, 25 (1954).

great difference in the radial variation of the attractive field acting on an electron in a negative ion and in a neutral atom or positive ion,[6] (the field falls off much more rapidly in a negative ion than in a neutral atom or positive ion where it is nearly coulombic for large r) it may be expected that such calculations will, in general, give an affinity that is appreciably in error no matter how well the relation used fits the neutral atom and positive ion term values. That this is indeed the case is well known.

In the present paper we attempt to mitigate the consequences of the difference in form of the radial variation of the potential of negative ions as compared to that of atoms and positive ions by proposing a method of calculation that amounts essentially to the extrapolation of one known electron affinity in each period to give the affinities of the remaining elements in that period. While we cannot give a satisfying theoretical basis for the assumption on which the calculations are based, the empirical justification will be seen to be sufficient to demonstrate the usefulness of the proposal. The new method of estimation seems to have the important advantage of not being restricted to the elements of the first two rows of the Periodic Table.

THE METHOD OF ESTIMATION

Consider an atom or ion of atomic number Z containing N electrons. Let us assign to each of the electrons, in accordance with the Pauli principle, a set of values of the four quantum numbers n, l, m_l, and m_s. We refer to this assignment as the "configuration" of the N electrons. Let $E_\eta\ (Z, N)$ be the energy required to remove the electron in state η from the (Z, N) system in the given configuration, *without any other change taking place in the electronic configuration*. By the "state of an electron" we mean the values of the four quantum numbers n, l, m_l, and m_s for the electron *and also* whether or not the electron is paired.*

If a proton is added to the nucleus of the (Z, N) system to form the $(Z + 1, N)$ system with the same electronic configuration, the removal energy, $E_\eta(Z, N)$ of the electron in state η is altered. Thus, if $E_\eta(Z + 1, N)$ represents the removal energy of the electron in state η from the $(Z + 1, N)$ system, the quantity

$$\Delta E_\eta(Z, N) = E_\eta(Z + 1, N) - E_\eta(Z, N) \tag{1}$$

represents the change in the removal energy of the electron in state η which accompanies the process

$$(Z, N) \text{ system} + \text{nuclear proton} = (Z + 1, N) \text{ system}. \tag{2}$$

The (Z, N) and $(Z + 1, N)$ systems are taken to have the same electronic configuration. The value of $\Delta E_\eta(Z, N)$, for a given Z and N, depends on η and on the electronic configuration.

Let ε be an occupied electron state in the (Z, N) and $(Z + 1, N)$ systems which differs from η in one or more of n, l, and m_l (m_s may or may not be the same).† Consider the systems $(Z, N - \varepsilon)$ and $(Z + 1, N - \varepsilon)$ which differ, respectively, from the (Z, N) and $(Z + 1, N)$ systems *only* in lacking an electron in state ε. Let $E_\eta(Z, N - \varepsilon)$

* Actually, of course, if we know n, l, m_l, and m_s for an electron in an atomic system of known configuration we can tell whether or not it is paired.

† We do not allow the case in which ε differs from η *only* in m_s, since, when this is true, the designation of ε (i.e., its n, l, m_l, m_s, *and state of pairing*) depends on whether or not η is occupied and vice versa.

[6] H. S. W. MASSEY, *Negative Ions*. Cambridge University Press, London (1950).

and $E_\eta(Z+1, N-\varepsilon)$ be the removal energies for the electron in state η from these systems. Then,

$$\Delta E_\eta(Z, N-\varepsilon) = E_\eta(Z+1, N-\varepsilon) - E_\eta(Z, N-\varepsilon) \tag{3}$$

represents the change in the removal energy of the electron in state η associated with the process

$$(Z, N-\varepsilon) \text{ system} + \text{nuclear proton} = (Z+1, N-\varepsilon) \text{ system}. \tag{4}$$

The $(Z, N-\varepsilon)$ and $(Z+1, N-\varepsilon)$ systems are taken to have the same electronic configuration.

All of the above considerations have been for the purpose of writing the following definition:

$$P_{\varepsilon,\eta}(Z, N) = \Delta E_\eta(Z, N-\varepsilon) - \Delta E_\eta(Z, N). \tag{5}$$

$P_{\varepsilon,\eta}(Z, N)$ may be interpreted to represent the effect of the presence of the electron in state ε upon the value of $\Delta E_\eta(Z, N)$. For a given Z and N the value of $P_{\varepsilon,\eta}(Z, N)$ depends on ε, η, and the configuration of the (Z, N) system.

If the (Z, N) system is taken to be a negative ion with a configuration whose energy level corresponds to the spectroscopic ground state, then $E_\eta(Z, N)$ will be the electron affinity of the $(Z, N-\eta)$ atom, that is, the electron affinity of the ground state of the $(Z, N-1)$ atom *plus* the relative energy level (i.e., the energy level relative to the ground state energy level taken as zero) of the $(Z, N-\eta)$ atom. We shall now find a way of estimating $P_{\varepsilon,\eta}(Z, N)$ for negative ions. Then for those cases in which the relative energy level of the $(Z, N-\eta)$ atom and all the removal energies in (5), except $E_\eta(Z, N)$, are known, we can calculate the electron affinity of the ground state of the $(Z, N-1)$ atom.

Let us first take the (Z, N) system to be a neutral atom, so that the ionization potentials and energy levels for calculating $P_{\varepsilon,\eta}(Z, N)$ from equation (5) are, in many cases, available. For a given (Z, N) we must first of all decide for which ε and η we shall make the calculation. While in principle any occupied ε and η in the atom can be chosen, in practice the choice is restricted by the availability of the necessary energy level values to only a few outer electron states. Having selected ε and η, we must next decide what configuration of the (Z, N) system to use. The simplest thing to do is to choose that configuration, with occupied states ε and η, whose energy level is the lowest.* This is what was done in obtaining the $P_{\varepsilon,\eta}(Z, N)$ values given in Tables 1 and 2. It may be noted that it is in general possible to write more than one configuration with the same energy level; however, it turns out that, for all of the electron states ε and η for which we calculate P, in only one of these configurations are both ε and η occupied. There is, therefore, no ambiguity in the calculations of $P_{\varepsilon,\eta}(Z, N)$.

Before discussing the numbers in Tables 1 and 2, we give as an illustration the

* This will not always be the configuration whose energy level is the spectroscopic ground state; in fact it is not always possible to write a configuration whose energy level is the same as the spectroscopic ground state level. In these cases the configuration whose energy level most nearly approximates the ground state level is used. Thus for B^- and C, the spectroscopic ground state level is $2p^3\ {}^2P_0$; but the nearest we can come to this is the configuration with $M_L = -1$, $M_S = +1$, and $M_J = 0$ (Cf. Table 1), the energy level of which is a linear combination of ${}^3P_2$, ${}^3P_1$ and ${}^3P_0$. In the calculations in this paper, whenever such a linear combination of levels with the same L and S but different J occurs, we make the approximation of using the centre of gravity instead of the correct linear combination. The resulting error is negligible. When a configuration whose energy level is a linear combination of levels with different L and S occurs we use the correct linear combination, as given by BACHER and GOUDSMIT.[4] This latter situation never arises for the N electron systems, but does several times for the N-ε and N-η systems.

TABLE 1.—$P_{\varepsilon,\eta}(Z, N)$ VALUES FOR NEUTRAL ATOMS, CALCULATED FROM EQUATION (5)*

(Z, N) system	Electronic configuration and energy level designation of (Z, N) system†	$P_{\varepsilon,\eta}(Z, N)$ (eV)				
		‡ $\varepsilon = 2s\,0 - \frac{1}{2}\,pd.$ $\eta = 2p - 1 + \frac{1}{2}\,u.$	$\varepsilon = 2p\,0 + \frac{1}{2}\,u.$ $\eta = 2p - 1 + \frac{1}{2}\,u.$	$\varepsilon = 2p - 1 + \frac{1}{2}\,u.$ $\eta = 2p + 1 - \frac{1}{2}\,pd.$	$\varepsilon = 2s\,0 - \frac{1}{2}\,pd.$ $\eta = 2p + 1 - \frac{1}{2}\,pd.$	$\varepsilon = 2p\,0 + \frac{1}{2}\,pd.$ $\eta = 2p + 1 + \frac{1}{2}\,pd.$
B	$2p\ ^2P^\circ$(C.G.)	4·78				
C	$2p^2\ ^3P$(C.G.)	4·79	4·70			
N	$2p^3\ ^4S^\circ_{3/2}$	4·83	4·71 (5)			
O	$2p^4\ ^3P_2$	4·71	4·71	5·27	3·91	
F	$2p^5\ ^2P^\circ_{3/2}$	4·8 ± 0·1		5·3 ± 0·1	3·9 ± 0·1	4·8 ± 0·1
Ne	$2p^6\ ^1S_0$				3·85	4·84
		$\varepsilon = 3s\,0 - \frac{1}{2}\,pd.$ $\eta = 3p - 1 + \frac{1}{2}\,u.$	$\varepsilon = 3p\,0 + \frac{1}{2}\,u.$ $\eta = 3p - 1 + \frac{1}{2}\,u.$	$\varepsilon = 3p - 1 + \frac{1}{2}\,u.$ $\eta = 3p + 1 - \frac{1}{2}\,pd.$	$\varepsilon = 3s\,0 - \frac{1}{2}\,pd.$ $\eta = 3p + 1 - \frac{1}{2}\,pd.$	$\varepsilon = 3p\,0 + \frac{1}{2}\,pd.$ $\eta = 3p + 1 + \frac{1}{2}\,pd.$
Al	Same as B, $3p\ ^2P^\circ$(C.G.)	2·39				
Si	Same as C, $3p^2\ ^3P$(C.G.)	2·63	2·29			
P	Same as N, $3p^3\ ^4S^\circ_{3/2}$	—	2·4 ± 0·1			
S	Same as O, $3p^4\ ^3P_2$	2·6 ± 0·1	2·4 ± 0·1	2·7 ± 0·1	—	
Cl	Same as F, $3p^5\ ^2P^\circ_{3/2}$	—		2·68	2·32	2·46
A	Same as Ne, $3p^6\ ^1S_0$				—	2·2
		$\varepsilon = 4s\,0 - \frac{1}{2}\,pd.$ $\eta = 4p - 1 + \frac{1}{2}\,u.$	$\varepsilon = 4p\,0 + \frac{1}{2}\,u.$ $\eta = 4p - 1 + \frac{1}{2}\,u.$	$\varepsilon = 4p - 1 + \frac{1}{2}\,u.$ $\eta = 4p + 1 - \frac{1}{2}\,pd.$	$\varepsilon = 4s\,0 - \frac{1}{2}\,pd.$ $\eta = 4p + 1 - \frac{1}{2}\,pd.$	$\varepsilon = 4p\,0 + \frac{1}{2}\,pd.$ $\eta = 4p + 1 + \frac{1}{2}\,pd.$

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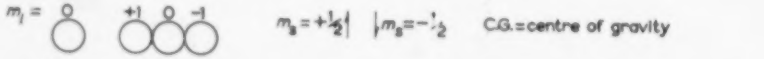
Ga	Same as B, $4p\ ^2P^\circ$(C.G.)	1·98				
Ge	Same as C, $4p^2\ ^3P$(C.G.)	—	1·5			
As	Same as N, $4p^3\ ^4S^\circ_{3/2}$	—	1·5			
Se	Same as O, $4p^4\ ^3P_2$	—	2·5	2·6	—	
Br	Same as F, $4p^5\ ^2P^\circ_{3/2}$	—		—	—	2·5
		$\varepsilon = 5s\,0 - \frac{1}{2}\,pd.$	$\varepsilon = 5p\,0 + \frac{1}{2}\,u.$	$\varepsilon = 5p - 1 + \frac{1}{2}\,u.$	$\varepsilon = 5s\,0 - \frac{1}{2}\,pd.$	$\varepsilon = 5p\,0 + \frac{1}{2}\,pd.$
		$\eta = 5p - 1 + \frac{1}{2}\,u.$	$\eta = 5p - 1 + \frac{1}{2}\,u.$	$\eta = 5p + 1 - \frac{1}{2}\,pd.$	$\eta = 5p + 1 - \frac{1}{2}\,pd.$	$\eta = 5p + 1 + \frac{1}{2}\,pd.$
In	Same as B, $5p\ ^2P^\circ$(C.G.)	1·6				
Sn	Same as C, $5p^2\ ^3P$(C.G.)	1·1 ± 0·5	0·9 ± 0·5			
I	Same as F, $5p^5\ ^2P^\circ_{3/2}$	—		—	—	2·20

* Data for all calculations with the exception of the ionization potentials of Nb^+, K^{++}, Ne^{++} and As^+ were taken from tables by MOORE[7] or LANDOLT and BÖRNSTEIN.[8] The ionization potentials for Nb^+, K^{++}, Ne^{++} and As^+ given by FINKELNBURG and HUMBACH[9] were preferred to those of MOORE who gives only a rough estimate for Nb^+, K^{++} and Ne^{++}, while the $I(As^+)$ listed by MOORE leads to zero value for P(As) and P(Ge).

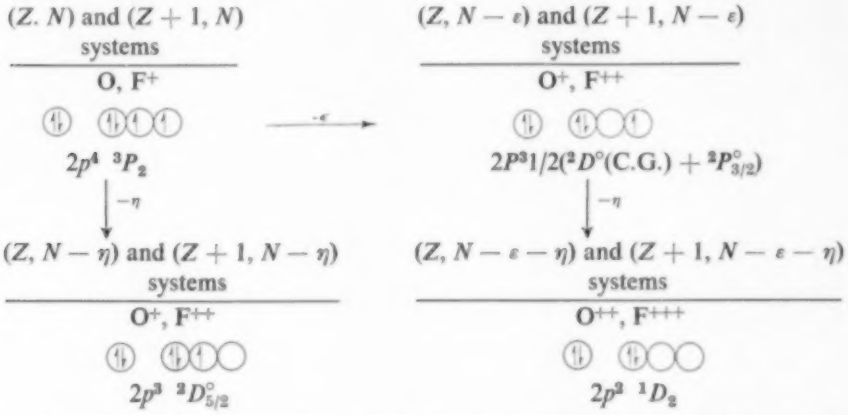
† The following conventions are followed in the configuration diagrams throughout the paper:



‡ Electron states are indicated by writing the quantum numbers n, l, m_l, and m_s followed by *pd.* or *u.* standing, respectively, for paired and unpaired.

[7] C. E. MOORE, *Atomic Energy Levels* Vols. I, II, circular 467. National Bureau of Standards, Washington.
[8] LANDOLT and BÖRNSTEIN, *Numerical Values and Functions from Physics, Chemistry, Astronomy, Geophysics, and Technology Atomic and Molecular Physics, Part I—Atoms and Ions.* Springer–Verlag, Berlin (1950).
[9] W. FINKELNBURG and W. HUMBACH, *Naturwissenschaften* **42**, 35 (1955).

details of the calculation of $P_{\varepsilon,\eta}(O)$ for $\varepsilon = 2p\ 0 + \frac{1}{2}\ u$, $\eta = 2p - 1 + \frac{1}{2}\ u$. (See footnotes to Table 1 for the conventions used in designating electron states and in drawing electron configuration diagrams.)


(Z. N) and (Z + 1, N) systems
O, F+
2p4 3P2
(Z, N − ε) and (Z + 1, N − ε) systems
O+, F++
2P3 1/2(2D°(C.G.) + 2P°3/2)
−ε
−η
−η
(Z, N − η) and (Z + 1, N − η) systems
O+, F++
2p3 2D°5/2
(Z, N − ε − η) and (Z + 1, N − ε − η) systems
O++, F+++
2p2 1D2

Using I to represent the ground state ionization potential and the energy level designation to represent the *relative* energy level, we have for the removal energies,

$$E_\eta(Z, N) = I(O) + 2p^3\ {}^2D^\circ_{5/2}(O^+) - 2p^4\ {}^3P_2(O) = 16{\cdot}937\ \text{eV},$$

$$E_\eta(Z + 1, N) = I(F^+) + 2p^3\ {}^2D^\circ_{5/2}(F^{++}) - 2p^4\ {}^3P_2(F^+) = 39{\cdot}20\ \text{eV},$$

$$E_\eta(Z + 1, N - \varepsilon) = I(F^{++}) + 2p^2\ {}^1D_2(F^{+++}) - 2p^3 1/2({}^2D^\circ(\text{C.G.}) + {}^2P^\circ_{3/2}((F^{++}) = 60{\cdot}466\ \text{eV},$$

and

$$E_\eta(Z, N - \varepsilon) = I(O^+) + 2p^2\ {}^1D_2(O^{++}) - 2p^3\ 1/2({}^2D^\circ(\text{C.G.}) + {}^2P^\circ_{3/2})(O^+) = 33{\cdot}489\ \text{eV}.$$

Hence,

$$P_{\varepsilon,\eta}(O) = (60{\cdot}466 - 33{\cdot}489(- (39{\cdot}20 - 16{\cdot}937) = 4{\cdot}71\ \text{eV}.$$

For atoms not included in the tables there is, in general, insufficient data for calculating $P_{\varepsilon,\eta}$. The few such additional calculations that can be carried out do not affect the following discussion at all. A dash in the tables indicates that the corresponding calculation cannot be carried through because of missing data. A blank space means that the calculation is impossible with the (Z, N) configuration used.

Examination of Tables 1 and 2 shows that, for a given ε and η, $P_{\varepsilon,\eta}(Z, N)$ is approximately independent of the (Z, N) system. The agreement with this generalization is not equally good in all cases, but the only really large discrepancy is for $\varepsilon = 4p\ 0 + \frac{1}{2}\ u.$, $\eta = 4p - 1 + \frac{1}{2}\ u.$ in which case $P_{\varepsilon,\eta}$(Se) is 1 eV higher than $P_{\varepsilon,\eta}$(Ge) and $P_{\varepsilon,\eta}$(As). It seems reasonable to believe, however, that this discrepancy is caused by errors in some of the ionization potentials involved in the calculations—there appears to be considerable uncertainty in several of the values used. It is most likely that the calculated $P_{\varepsilon,\eta}$(Ge) and $P_{\varepsilon,\eta}$(As) are too low while $P_{\varepsilon,\eta}$(Se) is too high.

The 0·3 eV difference between $P_{\varepsilon,\eta}$(Cl) and $P_{\varepsilon,\eta}$(A), for $\varepsilon = 3p\ 0 + \frac{1}{2}\ pd.$, $\eta = 3p + 1 + \frac{1}{2}\ pd.$, is not in very good agreement with our generalization; but

since the calculation of $P_{\varepsilon,\eta}$(A) makes use of $I(K^{++})$, the value of which is uncertain, we do not take this discrepancy seriously. It should also be noted that in calculating $P_{\varepsilon,\eta}$(Si), for $\varepsilon = 3s\,0 - \frac{1}{2}\,pd.$, $\eta = 3p - 1 + \frac{1}{2}\,u.$, the value of $3s3p^2\ ^4P$ for Si^+ is needed. According to Moore[7] this has been determined only approximately, and the quoted value may have a "considerable uncertainty". Hence the value in Table 1 for this $P_{\varepsilon,\eta}$(Si) is not as accurate as implied by the number of significant figures given.

On the basis of Tables 1 and 2 we feel justified in making the following statement: When the (Z, N) system is a neutral atom, $P_{\varepsilon,\eta}(Z, N)$ is, for a given ε and η, approximately (in most cases to 0·1 eV or better) independent of the (Z, N) system, providing the (Z, N) system has that one of the possible configurations, with occupied states ε and η, whose energy level is the lowest.

TABLE 2.—FURTHER VALUES OF $P_{\varepsilon,\eta}(Z, N)$ FOR NEUTRAL ATOMS, CALCULATED FROM EQUATION (5)

(Z, N) system	Electronic configuration and energy level designation of (Z, N) system.*	$P_{\varepsilon,\eta}(Z, N)$ (eV)	
		$\varepsilon = 4s\,0 + \frac{1}{2}\,u.$ $\eta = 3d + 1 - \frac{1}{2}\,pd.$	$\varepsilon = 4s\,0 + \frac{1}{2}\,u.$ $\eta = 3d + 1 + \frac{1}{2}\,u.$
Sc	①○○○○ ① $3d^24s\ ^4F_{9/2}$		2·11
Ti	①①○○○ ① $3d^34s\ ^5F$(C.G. 5, 4)		—
V	①①①○○ ① $3d^44s\ ^6D$(C.G.)		1·96
Cr	①①①①○ ① $3d^54s\ ^7S_3$		2·08
Mn	①①①①① ① $3d^54s\ ^6D$(C.G. 9/2, 7/2)	2·19	
Fe	①①①①① ① $3d^74s\ ^5F_5$	2·19	
Co	①①①①① ① $3d^84s\ ^4F_{9/2}$	2·17	
Ni	①①①①① ① $3d^94s\ ^3D_3$	—	
Cu	①①①①① ① $3d^{10}4s\ ^2S_{1/2}$	2·18	

*m_l: +2 +1 0 −1 −2 0

We now make the *assumption* that the statement in the preceding paragraph is true also when the (Z, N) system is a negative ion. With this assumption we are in a position to evaluate $P_{\varepsilon,\eta}(Z, N)$ for many negative ions whose ground state ionization potential we do not know. Having done this we will, in many cases, be able to calculate the electron affinity of the corresponding atom from equation (5). The procedure is as follows: In each period one element must be selected whose electron affinity is accurately known. (This may be done in the second, third, fourth, and fifth periods, since the affinities of the halogens are reliably known.[10]) Using the known affinity, $P_{\varepsilon,\eta}(Z, N)$ is calculated for the ground state configuration of the negative ion of this element [equation (5)]. The states ε and η, for which the calculation of $P_{\varepsilon,\eta}$ is carried through, must be such that they are occupied in the ground state configuration of the negative ions of as many as possible of the other elements in the period. Our assumption then enables us to use the calculated $P_{\varepsilon,\eta}$ to find from equation (5) the affinities of these elements, provided, of course, the other ionization

[10] H. O. PRITCHARD, *Chem. Rev.* **52**, 529 (1953).

TABLE 3.—$P_{\varepsilon,\eta}(Z, N)$ VALUES FOR NEGATIVE IONS

(Z, N) system	Electronic configuration and energy level designation of (Z, N) system.	$P_{\varepsilon,\eta}(Z, N)$ (eV)				
		$\varepsilon = 2s\,0 - \frac{1}{2}\,pd.$ $\eta = 2p - 1 + \frac{1}{2}\,u.$	$\varepsilon = 2p\,0 + \frac{1}{2}\,u.$ $\eta = 2p - 1 + \frac{1}{2}\,u.$	$\varepsilon = 2p - 1 + \frac{1}{2}\,u.$ $\eta = 2p + 1 - \frac{1}{2}\,pd.$	$\varepsilon = 2s\,0 - \frac{1}{2}\,pd.$ $\eta = 2p + 1 - \frac{1}{2}\,pd.$	$\varepsilon = 2p\,0 + \frac{1}{2}\,pd.$ $\eta = 2p + 1 + \frac{1}{2}\,pd.$
F^-	$2p^6\ {}^1S_0$				4·61	5·70
O^-	$2p^5\ {}^2P^\circ_{3/2}$	5·50		5·92	4·61	5·70
N^-	$2p^4\ {}^3P_2$	5·50	5·37	5·92	4·61	
C^-	$2p^3\ {}^4S^\circ_{3/2}$	5·50	5·37			
B^-	$2p^2\ {}^3P$(C.G.)	5·50	5·37			
Be^-	$2p\ {}^2P^\circ$(C.G.)	5·50				
		$\varepsilon = 3s\,0 - \frac{1}{2}\,pd.$	$\varepsilon = 3p\,0 + \frac{1}{2}\,u.$	$\varepsilon = 3p - 1 + \frac{1}{2}\,u.$	$\varepsilon = 3s\,0 - \frac{1}{2}\,pd.$	$\varepsilon = 3p\,0 + \frac{1}{2}\,pd.$
		$\eta = 3p - 1 + \frac{1}{2}\,u.$	$\eta = 3p - 1 + \frac{1}{2}\,u.$	$\eta = 3p + 1 - \frac{1}{2}\,pd.$	$\eta = 3p + 1 - \frac{1}{2}\,pd.$	$\eta = 3p + 1 + \frac{1}{2}\,pd.$
Cl^-	Same as F^-, $3p^6\ {}^1S_0$				—	2·65
S^-	Same as O^-, $3p^5\ {}^2P^\circ_{3/2}$	—		2·88	2·40	2·65
P^-	Same as N^-, $3p^4\ {}^3P_2$	2·70	2·56	2·88	2·40	
Si^-	Same as C^-, $3p^3\ {}^4S^\circ_{3/2}$	2·70	2·56			
Al^-	Same as B^-, $3p^2\ {}^3P$(C.G.)	2·70	2·56			
Mg^-	Same as Be^-, $3p\ {}^2P^\circ$(C.G.)	2·70				
		$\varepsilon = 4s\,0 - \frac{1}{2}\,pd.$	$\varepsilon = 4p\,0 + \frac{1}{2}\,u.$	$\varepsilon = 4p - 1 + \frac{1}{2}\,u.$	$\varepsilon = 4s\,0 - \frac{1}{2}\,pd.$	$\varepsilon = 4p\,0 + \frac{1}{2}\,pd.$
		$\eta = 4p - 1 + \frac{1}{2}\,pd$	$\eta = 4p - 1 + \frac{1}{2}\,u.$	$\eta = 4p + 1 - \frac{1}{2}\,pd.$	$\eta = 4p + 1 - \frac{1}{2}\,pd.$	$\eta = 4p + 1 + \frac{1}{2}\,pd.$

Br^-	Same as F^-, $4p^6\ ^1S_0$				—	2·19
Se^-	Same as O^-, $4p^5\ ^2P^\circ_{3/2}$	—		2·39	—	2·19
As^-	Same as N^-, $4p^4\ ^3P_2$	2·36	2·09	2·39	—	
Ge^-	Same as C^-, $4p^3\ ^4S^\circ_{3/2}$	2·36	2·09			
Ga^-	Same as B^-, $4p^2\ ^3P$(C.G.)	2·36	2·09			
Zn^-	Same as Be^-, $4p\ ^2P^\circ$(C.G.)	2·36				
		$\varepsilon = 5s\,0 - \frac{1}{2}\,pd.$	$\varepsilon = 5p\,0 + \frac{1}{2}\,u.$	$\varepsilon = 5p - 1 + \frac{1}{2}\,u.$	$\varepsilon = 5s\,0 - \frac{1}{2}\,pd.$	$\varepsilon = 5p\,0 + \frac{1}{2}\,pd.$
		$\eta = 5p - 1 + \frac{1}{2}\,u.$	$\eta = 5p - 1 + \frac{1}{2}\,u.$	$\eta = 5p + 1 - \frac{1}{2}\,pd.$	$\eta = 5p + 1 - \frac{1}{2}\,pd.$	$\eta = 5p + 1 + \frac{1}{2}\,pd.$
I^-	Same as F^-, $5p^6\ ^1S_0$				—	1·75
Te^-	Same as O^-, $5p^5\ ^2P^\circ_{3/2}$	—		[1·90]*	—	1·75
Sb^-	Same as N^-, $5p^4\ ^3P_2$	—	1·55	[1·90]*	—	
Sn^-	Same as C^-, $5p^3\ ^4S^\circ_{3/2}$	—	1·55			
In^-	Same as B^-, $5p^2\ ^3P$(C.G.)	1·93	1·55			
Cd^-	Same as Be^-, $5p\ ^2P^\circ$(C.G.)	1·93				

* Estimated, see explanation in appendix.

potentials and energy level values are known. It turns out that in each period there are negative ions in whose ground state configuration no pair of states ε and η, for which $P_{\varepsilon,\eta}$ can be calculated using the known affinity, is occupied. For this type of ion we clearly cannot use the known $P_{\varepsilon,\eta}$ to calculate the affinity of the corresponding atom. What is needed for these ions is $P_{\varepsilon',\eta'}$ where ε' and η' are different (in the same sense as ε and η) occupied electron states in the ground state configuration. Now, if ε' and η' are properly chosen, there will be some negative ion (Z, N) in the period (*not* the negative ion whose experimental ionization potential has been used) in whose ground state configuration ε, ε', η, and η' are all occupied. Using L to represent a relative energy level, we may then write

$$\begin{aligned} P_{\varepsilon',\eta'}(Z, N) = P_{\varepsilon,\eta}(Z, N) &- [L(Z+1, N-\varepsilon-\eta) - L(Z+1, N-\varepsilon) \\ &- L(Z, N-\varepsilon-\eta) + L(Z, N-\varepsilon) - L(Z+1, N-\eta) \\ &+ L(Z, N-\eta)] + [L(Z+1, N-\varepsilon'-\eta') - L(Z+1, N-\varepsilon') \\ &- L(Z, N-\varepsilon'-\eta') + L(Z, N-\varepsilon') - L(Z+1, N-\eta') \\ &+ L(Z, N-\eta')]. \end{aligned} \tag{6}$$

The real difficulty in calculating $P_{\varepsilon',\eta'}$ lies in selecting ε' and η' so that all the necessary energy level values are known.

Essentially, the above procedure amounts to an extrapolation of one known affinity in each period to give the affinities of the other elements in that period. Values of $P_{\varepsilon,\eta}$ for negative ions, calculated from the affinities of the halogens as quoted by PRITCHARD,[10] are collected in Table 3. The electron affinities obtained using these $P_{\varepsilon,\eta}$ values are shown in the third column of Table 4. Details of the calculations are given in the appendix.

In making the calculations it was assumed that the ground state configuration of a negative ion is the same as that of the neutral atom with atomic number one greater. BATES[11] has pointed out that this may not always be true. Since the attractive field falls off much more rapidly with distance in a negative ion than in a neutral atom, the extent to which an outer orbital penetrates the core has a much greater effect on its energy. Hence there is an increased stabilization for orbitals of low azimuthal quantum number. Thus, it might be that in some negative ions an outer ns-orbital is deeper than the $(n-1)p$-orbital.

BATES has quadratically extrapolated spectroscopic data on $(n-1)p \rightarrow ns$ excitation energies, for isoelectronic positive ions and neutral atoms, to get $(n-1)p \rightarrow ns$ excitation energies for the corresponding negative ions of the second and third periods. He finds that for Be^- the $3s$-orbital is deeper than the $2p$, and for Mg^- the $4s$-orbital is deeper than the $3p$. For the other negative ions the $2p$ lies below the $3s$ and the $3p$ below the $4s$-orbital as is true in neutral atoms. We have repeated BATES' calculations and extended them to the fourth and fifth periods (where, however, the quadratic extrapolation is less accurate) using the latest spectroscopic data.[7,8] The results are shown in Table 5. The magnitude of the (absolute) errors in these extrapolated excitation energies is probably smaller than the errors in electron affinities obtained by means of the quadratic extrapolation, for the error in the predicted excitation

[11] D. R. BATES, *Proc. Roy. Irish Acad.* A **51**, 151 (1947).

TABLE 4.—ELECTRON AFFINITIES OF ATOMS

Atom	Energy level designation of negative ion	Estimated electron affinity (eV)*	Best experimental affinity (eV)	Reference for experimental affinity (Nos. refer to footnotes)	Affinity estimated by the quadratic extrapolation[10]
Be	$2p\ {}^2P^\circ_{1/2}$	−0·12			−0·81
Be	$3s\ {}^2S_{1/2}$	0·90			
B	$2p^2\ {}^3P_0$	0·56 ± 0·02	>0	16	−0·09
C	$2p^3\ {}^4S^\circ_{3/2}$	1·59 ± 0·01	~1·6	Estimated from (18)	0·83
N	$2p^4\ {}^3P_2$	−0·10 ± 0·04	≤0	19, 6	−0·10 ± 1·0
O	$2p^5\ {}^2P^\circ_{3/2}$	1·46 | 1·60 ± 1·74 | 0·14	1·48 ± 0·10	12	0·70
Mg	$3p\ {}^2P^\circ_{1/2}$	−0·56			−0·91
Mg	$4s\ {}^2S_{1/2}$	−0·24			
Al	$3p^2\ {}^3P_0$	0·43 ± 0·05	>0	16	0·50 ± 0·4
Si	$3p^3\ {}^4S^\circ_{3/2}$	1·63			2·70 ± 0·5
P	$3p^4\ {}^3P_2$	0·7(5)	>0	16	0·57
S	$3p^5\ {}^2P^\circ_{3/2}$	2·24	2·07 ± 0·07	16	2·17 ± 1·0
Zn	$4p\ {}^2P^\circ_{1/2}$	−0·90			
Zn	$5s\ {}^2S_{1/2}$	−0·13			
Ga	$4p^2\ {}^2P_0$	0·18 ± 0·04			
Ge	$4p^3\ {}^4S^\circ_{3/2}$	1·2			
As	$4p^4\ {}^3P_2$	0·6(5)			
Se	$4p^5\ {}^2P^\circ_{3/2}$	2·2	≥1·7	20	
Cd	$5p\ {}^2P^\circ_{1/2}$	−0·6			
Cd	$6s\ {}^2S_{1/2}$	0·0			
In	$5p^2\ {}^3P_0$	0·2			
Te	$5p^4\ {}^3P^\circ_{0/2}$	2·30	2·2	20	

* Where an uncertainty is indicated, it is just the average deviation of the mean of values calculated from $P_{\varepsilon,\eta}$ for different choices of ε and η. Uncertainties in the ionization potentials used and in the affinities of the halogens, upon which the calculations are based, are *not* included in the indicated uncertainties.

energy is due to the difference in the errors of the extrapolated affinities for state A and state B (presumably these errors are of the same sign).

According to Table 5, for Be^-, Mg^-, Zn^-, and Cd^-, state B is the ground state rather than state A as assumed in our electron affinity calculations. In Table 4 is given an estimate of the electron affinity of Be, Mg, Zn, and Cd, for state B as the ground state of the negative ion, obtained by subtracting the corresponding $p \rightarrow s$ excitation energy in Table 5 from the calculated affinity for state A as the negative ion ground state.

DISCUSSION OF RESULTS

For comparison with the calculated affinities there are given in the fourth column of Table 4 what appear at present to be the best experimental values. Where no experimental affinity is listed none could be found in the literature. To put the comparison between the calculated and experimental affinities in its proper perspective some comments will now be made on the reliability of the experimental results.

The value given for oxygen was obtained by BRANSCOMB and SMITH[12] in a study of electron photo-detachment from a beam of O^- ions. Their result is in marked disagreement with that of METLAY and KIMBALL,[13] who obtained $2{\cdot}33 \pm 0{\cdot}03$ eV for the electron affinity of atomic oxygen, from a study of electron attachment at a hot filament. In his review PRITCHARD accepted METLAY and KIMBALL's result as

TABLE 5.—$(n-1)p \rightarrow ns$ EXCITATION ENERGIES OF NEGATIVE IONS CALCULATED BY THE QUADRATIC EXTRAPOLATION

Negative ion	State A	State B	Excitation energy of $A \rightarrow B$ (eV).
Be^-	$2p\ ^2P^o_{1/2}$	$3s\ ^2S_{1/2}$	−1·02
B^-	$2p^2\ ^3P_0$	$3s\ ^3P^o_0$	0·19
C^-	$2p^3\ ^4S^o_{3/2}$	$3s\ ^4P_{1/2}$	1·34
N^-	$2p^4\ ^3P_2$	$3s\ ^5S^o_2$	0·68
O^-	$2p^5\ ^2P^o_{3/2}$	$3s\ ^4P_{5/2}$	1·98
F^-	$2p^6\ ^1S_0$	$3s\ ^3P^o_2$	4·09
Mg^-	$3p\ ^2P^o_{1/2}$	$4s\ ^2S_{1/2}$	−0·32
Al^-	$3p^2\ ^3P_0$	$4s\ ^3P^o_0$	0·74
Si^-	$3p^3\ ^4S^o_{3/2}$	$4s\ ^4P_{1/2}$	1·60
P^-	$3p^4\ ^3P_2$	$4s\ ^5S^o_2$	1·07
S^-	$3p^5\ ^2P^o_{3/2}$	$4s\ ^4P_{5/2}$	2·55
Cl^-	$3p^6\ ^1S_0$	$4s\ ^3P^o_2$	4·27
Zn^-	$4p\ ^2P^o_{1/2}$	$5s\ ^2S_{1/2}$	−0·76
Ga^-	$4p^2\ ^3P_0$	$5s\ ^3P^o_0$	0·3
Ge^-	$4p^3\ ^4S^o_{3/2}$	$5s\ ^4P_{1/2}$	1·4
As^-	$4p^4\ ^3P_2$	$5s\ ^5S^o_2$	1·0
Cd^-	$5p\ ^2P^o_{1/2}$	$6s\ ^2S_{1/2}$	−0·6
Hg^-	$6p\ ^2P^o_{1/2}$	$7s\ ^2S_{1/2}$	−0·5

the most accurate value for oxygen, principally because of the agreement between it and the results of electron impact experiments[14] which gave $2{\cdot}2 \pm 0{\cdot}2$ eV for A(O). More recently, however, HAGSTRUM[15] has shown that use of BRANSCOMB and SMITH's value for the affinity of oxygen permits, at least in part, a satisfactory interpretation of the electron impact data. In view of this, and the convincing nature of BRANSCOMB and SMITH's experiment, it appears that $1{\cdot}48 \pm 0{\cdot}10$ eV is now the best experimental value for A(O).

The experimental value given for sulphur was obtained by BRANSCOMB and SMITH[16] from measurements of electron photo-detachment currents from a beam of S^- ions and is probably reliable. Electron impact appearance potentials in sulphur dioxide give, according to ROSENBAUM and NEUERT,[17] a lower bound of $2{\cdot}2 \pm 0{\cdot}3$ eV for the sulphur affinity. The latter authors also obtained a lower bound of about 1·2 eV from carbon disulphide.

[12] L. M. BRANSCOMB and S. J. SMITH, *Phys. Rev.* **98**, 1127 (1955); *J. Res. Nat. Bur. Stand.* **55**, 165 (1955).
[13] M. METLAY and G. E. KIMBALL, *J. Chem. Phys.* **16**, 774 (1948).
[14] H. D. HAGSTRUM, *Rev. Mod. Phys.* **23**, 185 (1951).
[15] H. D. HAGSTRUM, *J. Chem. Phys.* **23**, 1178 (1955).
[16] L. M. BRANSCOMB and S. J. SMITH, *J. Chem. Phys.* **25**, 598 (1956).
[17] O. ROSENBAUM and H. NEUERT, *Z. Naturf.* **9** A, 990 (1954).

As a result of his mass spectrometric study of the sublimation of graphite, HONIG[18] obtained the result $A(C) \sim 1{\cdot}2$ eV. This is a rough value which, according to HONIG, is probably on the low side. There is some indication from HONIG's results that the value just quoted may be low by about one third. This would make the true $A(C) \sim 1{\cdot}6$ eV in excellent agreement with our calculated value. (MASSEY[6] has estimated that $A(C) \leq 1{\cdot}7$ eV and considered that 1·5 eV was the best value.)

Comparison of the calculated and experimental affinities indicates that the method of calculation is useful, and that the predicted affinities may be expected to be fairly reliable. This conclusion is also supported by the following considerations:

(1) The negative value calculated for $A(N)$ is in accord with the failure to observe negative ions of nitrogen in discharges in air.[19]

(2) The positive affinities calculated for boron, aluminium, and phosphorous are in accord with the known stability of the negative ions of these elements.[16]

(3) The calculated electron affinities for the atoms which possess three p electrons in their outer shells (nitrogen, phosphorous, and arsenic) are lower than those of the neighbouring atoms on either side. BATES[11] and MASSEY[6] have pointed out that this comparative ease of detachment of the fourth p electron is to be expected on simple theoretical grounds.

(4) The fact that the average deviation of the calculated affinities, which are the mean of values obtained from different choices for ε and η, is small (cf. Table 4) indicates (but, of course, does not guarantee) that our basic assumption is fairly accurate.

In the last column of Table 4 we give the affinities calculated by means of the GLOCKLER quadratic extrapolation which has been the most widely used method of estimating the electron affinities of atoms. The values listed were calculated by PRITCHARD[10] from the ionization potentials given by MOORE. It is clear that the affinities calculated by the method described in the present paper are in better agreement with the experimental values than those calculated by the quadratic extrapolation. We also see that in most cases the affinities calculated by our method are distinctly higher than the results of the quadratic extrapolation. This is in agreement with the idea favoured by BATES[11] that the quadratic extrapolation affinities should be regarded as lower limits. The only clear exception is silicon for which the quadratic extrapolation gives a much higher affinity than our method.

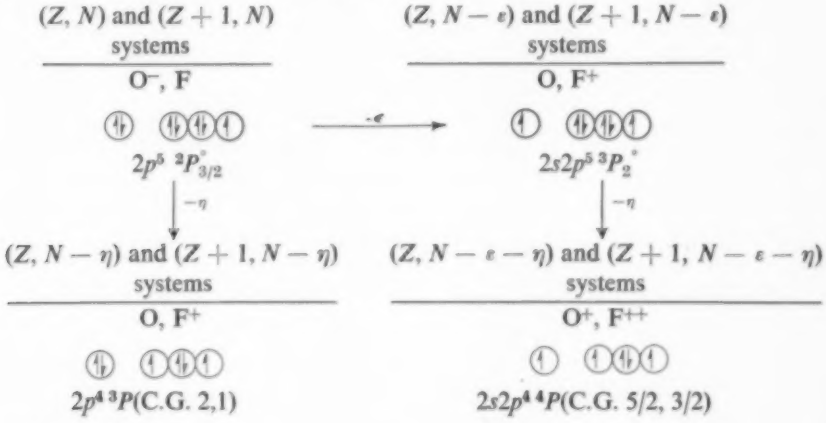
In conclusion it should be pointed out that in many cases we have not carried the calculations out for every possible choice of ε and η for which all the necessary data are available. However, in a few cases we carried out calculations for several *additional* choices of ε and η (not mentioned in the paper). Including the results of these additional calculations in the mean affinity brings about only a very small change from the value in Table 4. Because of this and the fact that the average deviations of the mean calculated affinities are so small, it seems reasonable to believe that if all of the additional possible calculations were carried out the results in Table 4 would only be changed slightly, probably in most cases by $<0{\cdot}1$ eV.

Acknowledgements—The authors wish to thank Dr. MAX WOLFSBERG for helpful discussions. One of us (A. P. G.) also wishes to thank the Monsanto Chemical Co. for a fellowship held during 1957–58.

[18] R. E. HONIG, *J. Chem. Phys.* **22**, 126 (1954).
[19] O. TÜXEN, *Z. Physik.* **103**, 463 (1936).

APPENDIX

The second period elements. Using the experimental $A(F) = 3{\cdot}62 \pm 0{\cdot}09$ eV, $P_{\varepsilon,\eta}$ (F^-, G.S. config.), for $\varepsilon = 2p\,0 + \frac{1}{2}\,pd.$, $\eta = 2p + 1 + \frac{1}{2}\,pd.$, and for $\varepsilon = 2s\,0 - \frac{1}{2}\,pd.$, $\eta = 2p + 1 - \frac{1}{2}\,pd.$, was obtained from equation (5). Both of these pairs of electron states are occupied in the ground state configuration of O^-. Hence we can make two independent calculations of the oxygen affinity (all the necessary energy levels are available in both cases). As an illustration of the method we give the details for the calculation of $A(O)$ using $\varepsilon = 2s\,0 - \frac{1}{2}\,pd.$, $\eta = 2p + 1 - \frac{1}{2}\,pd.$


(Z, N) and (Z + 1, N) systems
O⁻, F
(Z, N − ε) and (Z + 1, N − ε) systems
O, F⁺
−ε
2p⁵ ²P°3/2
2s2p⁵ ³P°2
−η
−η
(Z, N − η) and (Z + 1, N − η) systems
O, F⁺
(Z, N − ε − η) and (Z + 1, N − ε − η) systems
O⁺, F⁺⁺
2p⁴ ³P(C.G. 2,1)
2s2p⁴ ⁴P(C.G. 5/2, 3/2)

From (1), (3), and (5)

$$E_\eta(O^-) = P_{\varepsilon,\eta}(O^-) + E_\eta(Z + 1, N) + E_\eta(Z, N - \varepsilon) - E_\eta(Z + 1, N - \varepsilon).$$

Now,

$$E_\eta(Z + 1, N) = I(F) + 2p^4\,{}^3P(\text{C.G. } 2, 1)(F^+) = 17{\cdot}44,$$

$$E_\eta(Z, N - \varepsilon) = I(O) + 2s2p^4\,{}^4P(\text{C.G. } 5/2, 3/2)(O^+) - 2s2p^5\,{}^3P^\circ_2(O) = 12{\cdot}83,$$

$$E_\eta(Z + 1, N - \varepsilon) = I(F^+) + 2s2p^4\,{}^4P(\text{C.G. } 5/2, 3/2)(F^{++}) - 2s2p^5\,{}^3P^\circ_2(F^+) = 33{\cdot}41,$$

and, by our basic assumption,

$$P_{\varepsilon,\eta}(O^-) = P_{\varepsilon,\eta}(F^-) = 4{\cdot}61.$$

Hence,

$$E_\eta(O^-) = 1{\cdot}47 \text{ eV},$$

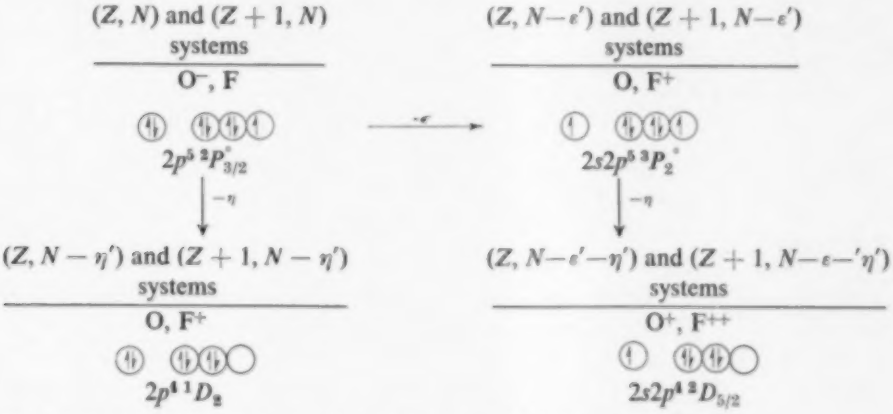
and

$$A(O) = E_\eta(O^-) - 2p^4\,{}^3P(\text{C.G.2, 1})(O) = 1{\cdot}47 - 0{\cdot}01 = 1{\cdot}46 \text{ eV}.$$

The other calculation of the oxygen affinity, based on $\varepsilon = 2p\,0 + \frac{1}{2}\,pd.$, $\eta = 2p + 1 + \frac{1}{2}\,pd.$, gives $A(O) = 1{\cdot}74$ eV. The discrepancy between the two results is due to the approximate nature of our basic assumption. As may be seen from Table 4, 1·46 eV is in better agreement with what is probably a good experimental value for $A(O)$ than is 1·74 eV. Hence, we derive the $P_{\varepsilon,\eta}$ values for the remaining first period elements *only* from the $P_{\varepsilon,\eta}(F^-)$ which gives $A(O) = 1{\cdot}46$ eV (i.e., $P_{\varepsilon,\eta}(F^-)$ for $\varepsilon = 2s\,0 - \frac{1}{2}\,pd.$, $\eta = 2p + 1 - \frac{1}{2}\,pd.$).

Using equation (6) we can now find $P_{\varepsilon',\eta'}(O^-)$ for several ε', η' for which a $P(F^-)$

cannot be obtained. Two useful possibilities are $\varepsilon' = 2s\,0 - \frac{1}{2}\,pd.$, $\eta' = 2p - 1 + \frac{1}{2}\,u.$, and $\varepsilon' = 2p - 1 + \frac{1}{2}\,u.$, $\eta' = 2p + 1 - \frac{1}{2}\,pd.$ (columns 3 and 5 of Table 3) To illustrate this type of calculation we give the details for the first ε', η' listed above.



On comparison with the preceding illustrative calculation, it is clear that

$$P_{\varepsilon',\eta'}(O^-) = 4{\cdot}61 - [2s2p^4\,{}^4P(\text{C.G.}5/2,\,3/2)(F^{++}) - 2s2p^5\,{}^3P_2^{\circ}(F^+)$$
$$- 2s2p^4\,{}^4P(\text{C.G.}5/2,\,3/2)(O^+) + 2s2p^5\,{}^3P_2^{\circ}(O) - 2p^4\,{}^3P(\text{C.G.}2,\,1)(F^+)$$
$$+ 2p^4\,{}^3P(\text{C.G.}2,\,1)(O)]\,[+ 2s2p^4\,{}^2D_{5/2}(F^{++}) - 2s2p^5\,{}^3P_2^{\circ}(F^+)$$
$$- 2s2p^4\,{}^2D_{5/2}(O^+) + 2s2p^5\,{}^3P_2^{\circ}(O) - 2p^4\,{}^1D_2(F^+) + 2p^4\,{}^1D_2(O)] = 5{\cdot}50\ \text{eV}.$$

We now have $P_{\varepsilon,\eta}$ for three choices of the pair of states ε and η (columns 3, 5 and 6 of Table 3) which can be used for calculating A(N). The result in Table 4 is the mean of these three calculations. From the $P_{\varepsilon,\eta}(N^-)$ for each of the three choices of the pair ε and η in columns 3, 5, and 6 we may calculate from equation (6) $P_{\varepsilon',\eta'}(N^-)$ for the ε', and η' of column 4, Table 3. The value given is the mean of the three calculations.

Of the choices of ε and η for which we now have $P_{\varepsilon,\eta}$ only the two of columns 3 and 4 can be used for calculating A(C) and A(B) while A(Be) may only be obtained from the $P_{\varepsilon,\eta}$ of column 3.

To calculate A(Li) we would have to take one of ε' and η' to be a $2s$ electron state and the other to be a $1s$ electron state. $P_{\varepsilon',\eta'}$ for such a choice of ε' and η' cannot be obtained from equation (6) because the necessary energy level values are not known. Similarly, we cannot find A(Ne) by our method because the energy level values for calculating $P_{\varepsilon',\eta'}$, for the proper choices of ε' and η', are not all available. For the same reason we can not obtain affinities for the other alkali metals and inert gases.

For B^- and Be^- the removal energies, $E_\eta(B^-)$ and $E_\eta(Be^-)$, which our calculations give, are related to the electron affinities as follows (assuming that the ground state of B^- is $2p^2\,{}^3P_0$ and that of Be^- is $2p\,{}^2P^{\circ}_{1/2}$):

$$E_\eta(B^-) = A(B) + 2p\,{}^2P^{\circ}(\text{C.G.})(B) - 2p^2\,{}^3P(\text{C.G.})(B^-),$$
$$E_\eta(Be^-) = A(Be) + 2s^2\,{}^1S_0(Be) - 2p\,{}^2P^{\circ}(\text{C.G.})(Be^-).$$

From an examination of the corresponding relative energy level differences in the atom and positive ions isoelectronic with B^- and Be^-, respectively, it is found that

$$2p\,^2P^\circ(\text{C.G.})(\text{B}) - 2p^2\,^3P(\text{C.G.})(\text{B}^-) \leqslant 0{\cdot}001 \text{ eV},$$

and

$$2s^2\,^1S_0(\text{Be}) - 2p\,^2P^\circ(\text{C.G.})(\text{Be}^-) \leqslant 0{\cdot}001 \text{ eV}.$$

Neglecting these small quantities we have that

$$A(\text{B}) = E_\eta(\text{B}^-)$$

and

$$A(\text{Be}) = E_\eta(\text{Be}^-).$$

The third period elements. The calculations are analogous to those for the second period elements except that $P_{\varepsilon,\eta}(\text{Cl}^-)$ for $\varepsilon = 3s\,0 - \frac{1}{2}\,pd.$, $\eta = 3p + 1 - \frac{1}{2}\,pd.$ cannot be evaluated because some of the necessary energy level values are not known. Hence we base the calculations for this period on $P_{\varepsilon,\eta}(\text{Cl}^-)$ for $\varepsilon = 3p\,0 + \frac{1}{2}\,pd.$, $\eta = 3p + 1 + \frac{1}{2}\,pd.$ (column 7 of Table 3), calculated from $A(\text{Cl}) = 3{\cdot}82 \pm 0{\cdot}06$ eV. Using this, $A(\text{S})$ is calculated and by means of equation (6) $P_{\varepsilon',\eta'}(\text{S}^-)$ for $\varepsilon' = 3s\,0 - \frac{1}{2}\,pd.$, $\eta' = 3p + 1 - \frac{1}{2}\,pd.$, and for $\varepsilon' = 3p - 1 + \frac{1}{2}\,u.$, $\eta' = 3p + 1 - \frac{1}{2}\,pd.$ (columns 6 and 5 of Table 3). Only for the last mentioned choice of ε' and η' are all the necessary energy level values available to allow the calculation of $A(\text{P})$ from the corresponding $P_{\varepsilon',\eta'}$. Also, from this $P_{\varepsilon',\eta'}$ we calculate with equation (6) $P_{\varepsilon'',\eta''}(P^-)$ for $\varepsilon'' = 3s\,0 - \frac{1}{2}\,pd.$, $\eta'' = 3p - 1 + \frac{1}{2}\,u.$, and for $\varepsilon'' = 3p\,0 + \frac{1}{2}\,u.$, $\eta'' = 3p - 1 + \frac{1}{2}\,u.$ (columns 3 and 4 of Table 3). The remaining calculations are exactly analogous to the corresponding ones in the second period.

Examination of the corresponding energy level differences in the atom and positive ions isoelectronic with, respectively, Al^- and Mg^- indicates that

$$3p\,^2P^\circ(\text{C.G.})(\text{Al}) - 3p^2\,^3P(\text{C.G.})(\text{Al}^-) < 0{\cdot}01 \text{ eV},$$

and

$$3s^2\,^1S_0(\text{Mg}) - 3p\,^2P^\circ(\text{C.G.})(\text{Mg}^-) \leqslant 0{\cdot}01 \text{ eV}.$$

Neglecting these small quantities and assuming the ground states of Al^- and Mg^- to be $3p^2\,^3P_0$ and $3p\,^2P^\circ_{1/2}$, respectively, we have (cf. B^- and Be^-)

$$A(\text{Al}) = E_\eta(\text{Al}^-)$$

and

$$A(\text{Mg}) = E_\eta(\text{Mg}^-).$$

The fourth period elements. The calculations from Br^- to Zn^- are analogous to those for the corresponding third period elements. The experimental affinity used is $A(\text{Br}) = 3{\cdot}54 \pm 0{\cdot}06$ eV.

Using the energy levels given by MOORE[7] $P_{\varepsilon,\eta}(\text{As}^-)$, for $\varepsilon = 4s\,0 - \frac{1}{2}\,pd.$, $\eta = 4p - 1 + \frac{1}{2}\,u.$, comes out to be 1·45 eV. This leads to an absurd value for $A(\text{Ga})$,* which differs greatly from the value based on $P_{\varepsilon,\eta}(\text{As}^-)$ for $\varepsilon = 4p\,0 + \frac{1}{2}\,u.$, $\eta = 4p - 1 + \frac{1}{2}\,u.$ (Table 3, column 4). However, if instead of the value listed by MOORE for $4s4p^4\,^4P_{5/2}(\text{As})$, the value given by RAO[21] (62748 cm^{-1} relative to

* Because of missing energy level values this $P_{\varepsilon,\eta}$ cannot be used to calculate $A(\text{Ge})$.

[20] V. M. DUKEL'SKII and N. I. IONOV, *Dokl. Akad. Nauk SSSR* **81**, 767 (1951); (Quoted by PRITCHARD[10].)

[21] A. S. RAO, *Proc. Phys. Soc.* **44**, 594 (1932).

$4p^3\ {}^4S^\circ_{3/2}(\mathrm{As}) = 0$) is used, we get for the first mentioned $P_{\varepsilon,\eta}(\mathrm{As}^-)$ the result in column 3 of Table 3. The latter gives an $A(\mathrm{Ga})$ in excellent agreement with that obtained from the $P_{\varepsilon,\eta}(\mathrm{As}^-)$ of column 4.

Examination of the corresponding energy level differences in the atom and positive ions isoelectronic with Ga^- and Zn^-, respectively, indicates that

$$4p\ {}^2P^\circ(\mathrm{C.G.})(\mathrm{Ga}) - 4p^2\ {}^3P(\mathrm{C.G.})(\mathrm{Ga}^-) \sim 0{\cdot}02\ \mathrm{eV},$$

and

$$4s^2\ {}^1S_0(\mathrm{Zn}) - 4p\ {}^2P^\circ(\mathrm{C.G.})(\mathrm{Zn}^-) \sim -0{\cdot}01\ \mathrm{eV}.$$

These are small enough to be neglected. Hence, assuming the ground states of Ga^- and Zn^- to be, respectively, $4p^2\ {}^3P_0$ and $4p\ {}^2P^\circ_{1/2}$, we write (cf. B^- and Be^-)

$$A(\mathrm{Ga}) = E_\eta(\mathrm{Ga}^-)$$

and

$$A(\mathrm{Zn}) = E_\eta(\mathrm{Zn}^-).$$

The affinities of the transition metals cannot be obtained by our present method since the energy level values needed to calculate $P_{\varepsilon',\eta'}$ by equation (6), for appropriate ε' and η', have not been reported.

The fifth period elements. The experimental affinity used is $A(\mathrm{I}) = 3{\cdot}24 \pm 0{\cdot}06$ eV. The calculations are analogous to the corresponding ones in the fourth period except for the following:

(1) Because no values could be found for the levels $5p^3\ {}^2D^\circ_{5/2}$, ${}^2D^\circ_{3/2}$, and ${}^2P^\circ_{3/2}$ of I^{++}, $P_{\varepsilon,\eta}(\mathrm{Te}^-)$ for $\varepsilon = 5p - 1 + \frac{1}{2}\,u.$, $\eta = 5p + 1 - \frac{1}{2}\,pd.$ (column 5 of Table 3) could *not* be evaluated. It is essential to have this $P_{\varepsilon,\eta}$ in order to calculate P for the other ε and η used in Table 3 for the fifth period elements. An estimate for this quantity of 1·90 eV fits in nicely with the qualitative regularities apparent in Table 3. It is unlikely that this estimate is in error by much more than $\pm 0{\cdot}05$ eV.

(2) The affinities of antimony and tin are not reported in Table 4 because the uncertainty in the ground state ionization potentials of Te^+ and Sb^+ is so great as to render the calculation valueless.

Examination of the corresponding energy level differences in the atom and positive ions isoelectronic with, respectively, In^- and Cd^- indicates that

$$5p\ {}^2P^\circ(\mathrm{C.G.})(\mathrm{In}) - 5p^2\ {}^3P(\mathrm{C.G.})(\mathrm{In}^-) \sim +0{\cdot}1\ \mathrm{eV},$$

and

$$5s^2\ {}^1S_0(\mathrm{Cd}) - 5p\ {}^2P^\circ(\mathrm{C.G.})(\mathrm{Cd}^-) \sim -0{\cdot}04\ \mathrm{eV}.$$

Hence, assuming the ground states of In^- and Cd^- to be, respectively, $5p^2\ {}^3P_0$ and $5p\ {}^2P^\circ_{1/2}$, we take (cf. B^- and Be^-)

$$A(\mathrm{In}) = E_\eta(\mathrm{In}^-) - 0{\cdot}1$$

and

$$A(\mathrm{Cd}) = E_\eta(\mathrm{Cd}^-) + 0{\cdot}04.$$

J. Inorg. Nucl. Chem., 1958, Vol. 7, pp. 368 to 377. Pergamon Press Ltd., London

THE THERMAL DECOMPOSITION OF IRRADIATED POTASSIUM PERMANGANATE

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Abstract—The thermal decomposition of whole and ground $KMnO_4$ crystals has been re-examined in an attempt to cause nucleation by pre-irradiation with thermal neutrons, γ-rays, and protons. Decompositions, after irradiations of the solid in the pile, hot-spot, and thermal column, yielded similar p–t plots. The induction period is shortened, and the maximum velocity increased. The acceleration of the decomposition by a reaction proceeding from "irradiation nuclei" appears to be independent of any reaction originating from the nuclei ordinarily operative in unirradiated material. A mechanism involving the annealing of point defects over the induction period is suggested. The activation energy for this process has been determined as 1·31 eV, indicating the migration of vacancies.

THE thermal decomposition of single whole crystals of $KMnO_4$ in the temperature range 200–225°C has been investigated.[1] The induction period which precedes rapid decomposition is shortened by grinding the crystals—the change being dependent on the degree of grinding. The decompositions of both whole and ground crystals are unaffected by pre-irradiation with ultra-violet light from a quartz–mercury arc for 60 min at a distance of 20 cm. Bombardment with electrons generated by an applied potential of 20 kV in oxygen at a pressure of 2×10^{-3} cm Hg also has no effect.[2] The energies involved in these irradiations are insufficient to produce atomic displacement, since using the Seitz value of 25 eV for the displacement energy, the minimum radiation energy required for the displacement by electrons of atoms in $KMnO_4$ is greater than 0·1 MeV.[3]

Atomic displacement, however, can be performed by fast neutrons in an atomic pile. This necessitates irradiation in or near the centre of the pile. The temperature of irradiation (200°C in BEPO) however precludes this. Alternatively, atomic displacements can be produced indirectly by the thermal neutrons present in a cooler part of the pile. If one considers the γ-ray energy for the change $^{55}Mn\ (n, \gamma)\ ^{56}Mn$ to be concentrated in a single ray of 8 MeV, the manganese nucleus will recoil with an energy of 600 eV.[4] This is above the threshold energy required for atomic displacement by such nuclei.

The aim was to damage the $KMnO_4$ by pre-irradiation with thermal neutrons, and thus produce nuclei from which decomposition might proceed. The displacement of atoms by γ-rays present in the pile was also anticipated.

[1] E. G. PROUT and F. C. TOMPKINS, *Trans. Faraday Soc.* **40**, 488 (1944).
[2] E. G. PROUT and F. C. TOMPKINS, Unpublished work (1944).
[3] G. H. KINCHIN and R. S. PEASE, *Reports on Progress in Physics*, Vol. 18, p. 1. Physical Society, London (1955).
[4] H. A. C. MCKAY, *Progress in Nuclear Physics*, Vol. 1, p. 168. Pergamon Press, London, New York (1950).

EXPERIMENTAL

The preparation of the $KMnO_4$ crystals, the apparatus, and the procedure used were as previously described.[1] Unless otherwise stated, the whole crystals weighed 10–12 mg and the ground material 11·5 mg. Normalization to a common pressure was done for comparative p–t plots.

Pile irradiations were performed in BEPO in a position near the outside. The specimens were sealed in silica ampoules and exposed to a thermal neutron flux of 2×10^{11} neutrons cm^{-2} sec^{-1} at an ambient temperature of $30 \pm 5°C$. The specimens were allowed to decay for 24 hr before decomposition. The γ-irradiations were carried out, at room temperature, in a ^{60}Co hot-spot of total activity 439 curies. The dose rate, as measured by ferrous–ferric methods, was $1·6 \times 10^6$ r.e.p. hr^{-1}. ^{60}Co emits γ-rays of 1·33 and 1·17 MeV.

Bombardment of whole crystals by 145 MeV protons was done in the Harwell cyclotron. The specimens were placed in thin aluminium containers with the maximum possible cooling. Pulses of 0·5 sec with 5 sec intervals were injected. The crystals were externally apparently unchanged after irradiation with protons for 3 min.

RESULTS

The results were reproducible. Using 12 mg of whole crystals and an irradiation time of 15 hr in BEPO, the decomposition at 224°C produced p–t plots which were virtually superimposable. Similar results were produced after 15 hr γ-irradiation of whole crystals.

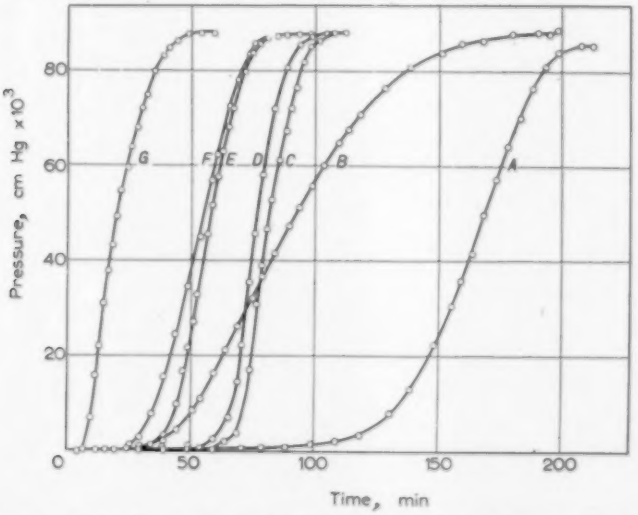

FIG. 1.—Curves showing effect of pre-irradiation on thermal decomposition at 215°C.
Whole crystals:
A—unirradiated; *C*—15 hr in BEPO; *D*—15 hr in γ-hot-spot; *G*—3 min in cyclotron.
Ground crystals:
B—unirradiated; *E*—15 hr in BEPO; *F*—15 hr in γ-hot-spot.

Fig. 1 shows the effects of pile, γ-, and cyclotron irradiation on both whole and ground specimens as compared with unirradiated specimens.

The progress of decomposition was independent of the mass of $KMnO_4$; using 6·3 mg and 12·2 mg crystals, the p–t curves obtained after a 15 hr pile irradiation were practically identical after a mass correction. Similar results were found after γ-irradiations. Visual observation of whole crystals after 15 hr γ- or pile irradiation, and decomposition at 215°C, showed that the crystal behaviour was similar to that of unirradiated crystals, except that there was greater splintering over the induction

period, and more rapid and violent disintegration over the acceleration period. In both cases the physical fracture ceased at the point of inflexion in the p–t plot. With a γ-irradiation of 168 hr the crystal virtually exploded at the end of the induction period and fracture was completed with this explosion.

The possibility of the damage in pile-irradiated material being continued after irradiation as a result of the change $^{56}Mn \xrightarrow[\gamma,\beta]{2{\cdot}59\ hr} {}^{56}Fe$, was studied. Whole crystals were irradiated for 4 hr. This gave the least decay during irradiation, and yet sufficient

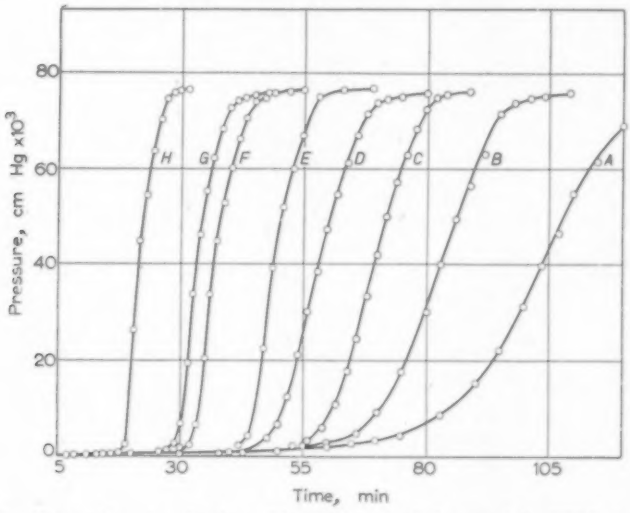

FIG. 2.—Effect of varying the time of irradiation of whole crystals in BEPO–decomposition temperature 224°C. Time of irradiation:
$A = 0$; $B = 10$ min; $C = 2$ hr; $D = 4$ hr; $E = 15$ hr, $F = 30$ hr; $G = 48$ hr; $H = 167$ hr.

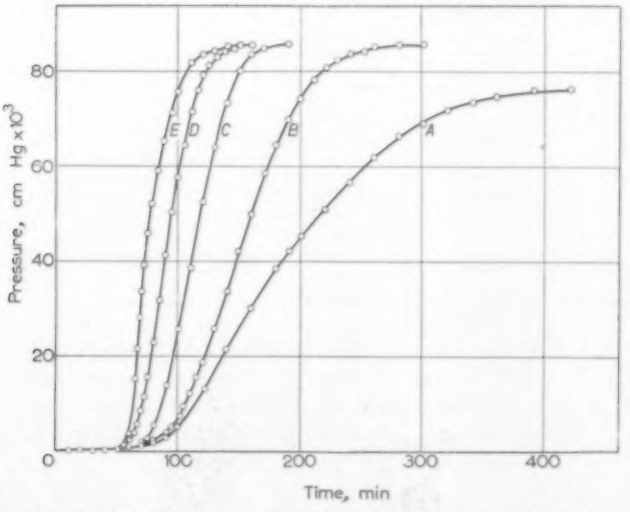

FIG. 3.—Showing the effect on ground crystals of varying times of irradiation in BEPO. Time of irradiation:
$A = 0$; $B = 2{\cdot}8$ hr; $C = 15$ hr; $D = 48$ hr; $E = 144$ hr.

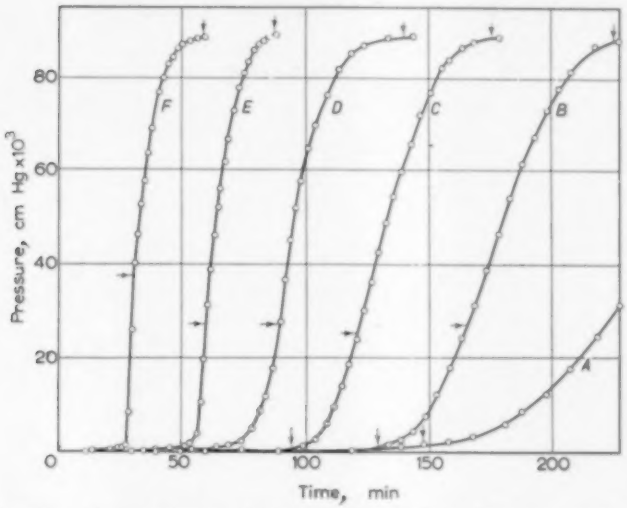

FIG. 4.—Effect of varying the time of irradiation of whole crystals in γ-hot-spot—decomposition temperature 210°C. Time of irradiation:
$A = 0$; $B = 10$ min; $C = 2$ hr; $D = 16\frac{1}{2}$ hr; $E = 72$ hr; $F = 168$ hr;
→ = Fit of equation (2).

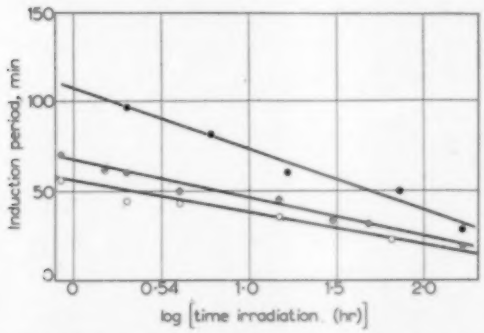

FIG. 5.—Relationship between induction period and time of irradiation.
● 210°C, γ-irradiation; ⊕ 224°C, pile irradiation; ○ 224°C, γ-irradiation.

activity at the end of the irradiation to produce measurable effects. Decompositions at 235°C were started at 50 min, 1½ hr, and 20 hr after irradiation. The p–t plots were practically identical.

Decompositions at a fixed temperature, after various times of pile irradiation, are shown in Figs. 2 and 3 for whole and ground crystals respectively. Similar runs with whole crystals after γ-irradiation are shown in Fig. 4. The variation of the length of the induction period for whole crystals could be represented by

$$\log (\text{time irradiation}) = kI + c \tag{1}$$

where I = length of induction period (Fig. 5).

The PROUT–TOMPKINS equation,

$$\log (p/(p_f - p)) = k't + c' \tag{2}$$

was applicable, after both γ- and pile irradiations, over the whole of the curve (excluding the induction period) for times of irradiation up to 15 hr.

Equation (2) was applicable over the decay period only, after pile or γ-irradiations of 15 hr or longer. Over the acceleration period the following expression held

$$\log p = k''t + c'' \tag{3}$$

TABLE 1.—γ-IRRADIATION

Temperature (°C)	k_1	k_2
200	0·02257	0·0070
205	0·0413	0·0445
210	0·0635	0·0759
215	0·110	0·0801
220	0·1418	0·1202
224	0·1972	0·1622
230	0·368	—

The fit of equation (2) is shown in Fig. (4). The analyses of the p–t plots after 15 hr irradiations are summarized in Tables 1 and 2. In Table 1 k_1 and k_2 refer to whole and ground respectively in the acceleration period wherein equation (3) is valid. In Table 2 k_3 and k_4 refer to whole and ground crystals respectively in the decay period where equation (2) is valid.

TABLE 2.—PILE IRRADIATIONS

Temperature (°C)	k_3	k_4
200	0·0207	—
205	—	0·2857
210	0·0526	0·4320
215	0·0757	0·6467
220	0·1080	0·9280
224	0·1440	—
225	—	1·347
230	0·2196	—

The log k against $1/T$ plots are well defined straight lines from which the activation energies E_1, E_2, E_3, and E_4 were obtained.

Table 3 compares these values to the corresponding ones previously obtained using unirradiated $KMnO_4$.

TABLE 3.—ACTIVATION ENERGIES

Irradiated	*Unirradiated*
E_1 40,300 cal/mole	38,534 cal/mole
E_2 32,000 cal/mole	34,550 cal/mole
E_3 34,500 cal/mole	38,842 cal/mole
E_4 36,300 cal/mole	33,110 cal/mole

The plot, log I against $1/T$ for irradiated specimens yielded straight lines (Fig. 6), from which activation energies were calculated. Pile irradiation for 15 hr of whole and ground crystals gave energies of 1·13 eV and 1·30 eV respectively. The values for γ-irradiation of 15 hr were 1·31 eV and 1·38 eV respectively.

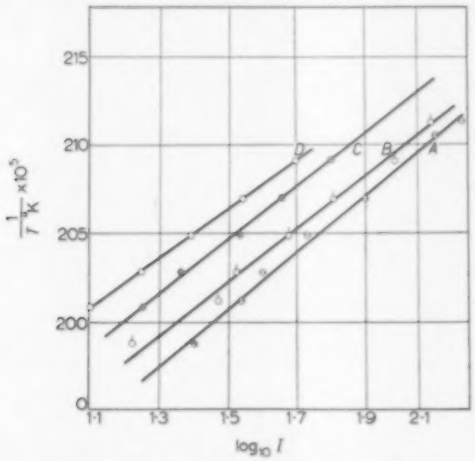

FIG. 6.—Activation energies over induction period.
Whole crystals:
A—irradiated 15 hr in BEPO; *B*—irradiated 15 hr in γ-hot-spot.
Ground crystals:
C—irradiated 15 hr in BEPO; *D*—irradiated 15 hr in γ-hot-spot.

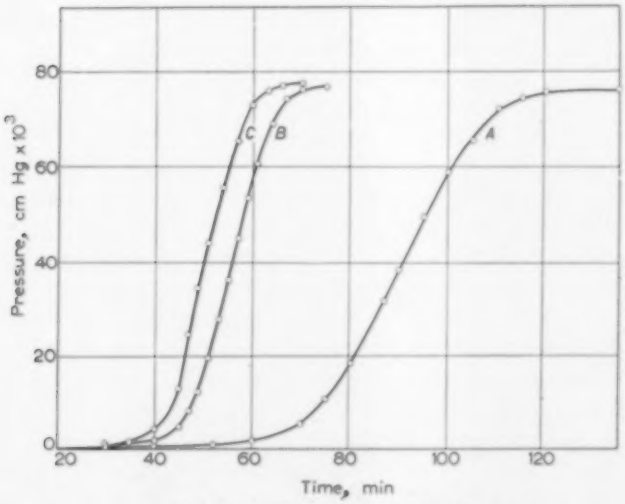

FIG. 7.—Irradiation in thermal column.
A—unirradiated; *B*—thermal column, 1 week; *C*—pile, 5 hr.

Irradiation with thermal neutrons only was done in the thermal column of BEPO at a flux of 7×10^9 neutrons cm^{-2} sec^{-1}. The crystal was placed in an A.R. Pb can and irradiated for 1 week which gave the same dose of thermal neutrons as 5 hr in the usual position in BEPO. The resulting p–t plot is shown in Fig. 7.

Whole crystals irradiated for 15 hr in both the γ-hot-spot and BEPO were annealed at 100°C in air for 213 hr. No effect on the subsequent decomposition at 215°C was observed, as compared to an irradiated, unannealed specimen.

The effect of interrupting the decomposition of an unirradiated whole crystal at a definite point in the decomposition, irradiating the specimen in the hot-spot or pile for a constant time, and then continuing the decomposition to completion, was studied. The results for pile irradiation are shown in Fig. 8. Similar results were obtained for γ-irradiated specimens.

DISCUSSION

The analysis of the results falls into three distinct sections: (a) the nature of the damage done during irradiation, (b) the process(es) occuring over the induction period, (c) the mechanism of the subsequent acceleration and decay.

Comparing the results obtained after irradiation of whole crystals in the pile (thermal neutrons and γ-rays), the thermal column, and the γ-hot-spot, it is apparent that the effective change is created by γ-rays, whether of capture or of radioactive decay. The last mentioned however, as is shown by the study of thermal decompositions shortly after irradiation, produces damage which is negligible compared with that produced in the pile.

The γ-rays from ^{60}Co have sufficient energy for some of the Compton and photoelectrons generated by them to exceed the threshold for atomic displacement. The cross-section for displacement is about 100 times smaller for an electron than a charged nucleon. Furthermore, since the collisions are heavily biased towards small energy transfer, the knocked-on atoms seldom have energy to produce secondaries. Consequently the simplest type of change will result; namely isolated pairs of vacancies and interstitials. DUGDALE[5] showed that disordering could be produced in Cu_3Au by means of ^{60}Co γ-radiation, and CLELAND *et al.*[6] have used the same radiation to produce displaced atoms in Ge. The displacement efficiency was found to be about 10^{-3} that of fast neutrons in the case of Ge.

It is considered here that the displacements of significance are those of K^+ ions into interstitial positions, and are brought about by Compton recoil electrons. The distance between the interstitial and the vacancy will rarely be more than four or five interatomic distances, and the effects will be randomly distributed in the crystal. The elevated temperature of the thermal decomposition will produce, over the induction period, an annealing of the point defects with the associated Wigner release of the stored energy. It has been assumed in the study of the energy stored in irradiated graphite that when an interstitial atom returns to a vacancy the energy released is ~10 eV.[7] The release of energy of a comparable magnitude in potassium permanganate, which is already at some temperature in the range 200–225°C, would cause the rupturing of bonds in the permanganate ions which are adjacent to the point of recombination of a interstitial-vacancy pair. Thus a centre of decomposed material will result.

[5] R. A. DUGDALE, *Report of Bristol Conference on Defects in Crystalline Solids*, p. 246. Physical Society, London (1955).
[6] J. W. CLELAND, J. H. CRAWFORD and D. K. HOLMES, *Bull. Amer. Phys. Soc.* **1**, 135 (1956); *Phys. Rev.* **102**, 722 (1956).
[7] G. H. KINCHIN, *Proceedings of International Conference on Peaceful Uses of Atomic Energy, Geneva*, 1955, Paper 442. United Nations (1956).

The recombination of interstitial-vacancy pairs has been discussed by FLETCHER and BROWN.[8] The reaction can be divided into three stages. The first is a unimolecular process within the deformed lattice around an interstitial and consists of the jumping of a vacancy. The second is a bimolecular process and is the movement of vacancies outside this distorted region where the vacancies move according to a random walk process. Some will wander back to the distorted region and recombine. In the third stage other vacancies will wander away and may become annihilated at defects or trapped at the surface or at dislocations. The annealing process will thus be time extended. The average jump time τ required for a vacancy to make a jump under thermal excitation, is given by $\tau = \nu_0^{-1} \exp E/kT$, where ν_0 is the average lattice frequency (ca. 10 c/s), and E is the potential barrier for a neighbouring atom to jump into a vacancy.[9] Vacancies near edge dislocations and especially near jogs in dislocations will be the first to combine with adjacent interstitials created by atomic displacement.

The presence of decomposition products around the postulated centre of decomposition in $KMnO_4$ will cause a deformation of the $KMnO_4$ lattice and may result in a lowering of the activation energy for a vacancy jump. There will thus be preferential annealing around this region which will increase in size to form a "decomposition spike". During the annealing period there will be an increase in the number of such centres, and a steady accumulation of strain in the crystal will result. This strain will be sufficient to produce physical fracture of the solid at the end of the induction period. This fracturing will occur throughout the crystal and the end of the induction period will mark the commencement of bulk disintegration. Similar work with $AgMnO_4$, as yet incomplete, shows that an unirradiated large single crystal retains its single crystal external morphology to the completion of the decomposition. Irradiated single crystals, however, undergo explosive fracturing at the end of the induction period which continues to the onset of the decay period.

The strain at various points within the crystal will not reach the critical disruptive value at exactly the same time. With moderate radiation doses, an extension of the fracturing process beyond the end of the induction period into the acceleration region will occur. With heavy doses, and consequent increase in the density of defects, the times between the attainment of critical strain will have decreased and the fracture process should be an instantaneous break-up of the crystal. The observed lowering of the inflexion point in the p–t plots (Fig. 4) is due to this.

FLETCHER and BROWN consider that, by comparing the times at which the same degree of annealing occurs for different temperatures, the barrier energy, E, can be determined without an actual fit of the theoretical expression to the experimental data. The variation with temperature of the length of the induction period, with a fixed time of irradiation, can be assumed to reflect the temperature dependence of the average jump time of the moving defect. This is possibly complicated by the change of the critical strain within the crystal with the decomposition temperature, but the effect should not be significant within the range studied i.e. 200–225°C. The plot of log I against $1/T$ for a fixed time of irradiation should yield a value for E. The average value of 1·31 eV found, indicates the migration of vacancies, which is to be expected in preference to interstitials on energy grounds. (The migration of

[8] R. C. FLETCHER and W. L. BROWN, *Phys. Rev.* **92**, 585 (1953).
[9] N. F. MOTT and R. W. GURNEY, *Electronic Processes in Ionic Crystals*. Oxford University Press (1950).

vacancies in cold worked Cu[10] and Mo[5] is associated with activation energies of 1·25 eV and 1·20–1·35 eV respectively).

The virtual elimination of the induction period with proton bombardment is due to the greater damage done by the fast particle in creating a larger number of secondary knock-ons. In this case the annealing effect will be very rapid due to a higher concentration of defects and the shortening of the jump time caused by lattice distortion.

Ground and whole crystals irradiated for the same time and decomposed at the same temperature have different induction periods with the induction period of the former the shorter. The rate of annealing in stage 1 is proportional to the number of close interstitial-vacancy pairs, and in stage 2 to the number of vacancies. It is reasonable to presume that the grinding will be similar to the cold working of metals which produces a high concentration of vacancies[11] and increases the number of dislocations.[12] There will therefore be a greater number of both close pairs and vacancies in irradiated ground material, and the induction period should be shorter than in whole crystal decompositions. The number of decomposition centres preferentially formed at dislocations will also be increased.

Fig. 3 shows that the length of the induction period for 48 and 144 hr irradiations is the same. This is attributed to a saturation of the number of interstitials formed with high dosage. With the initially large number of vacancies created by grinding there will be a point when with steadily increasing dosage virtually instantaneous recovery of the displaced atom will occur. Saturation effects have been observed with boron nitride[13] and zircon[14] subjected to neutron and α-particle bombardment respectively.

Unirradiated whole and ground crystal decompositions at a given temperature differ in, (a) the length of the induction period (b) the maximum velocity attained, and (c) the time of commencement of the decay period. In Fig. 1 however, it is seen that pre-irradiation for 15 hr yields decomposition curves which differ only in (a). It is assumed that the fracturing at the end of the induction period produces fragments with surfaces which are structurally alike in all cases and the ensuing decompositions are correspondingly similar.

Fig. 8 shows that the commencement of the reaction at the end of the induction period originates, in the two cases of unirradiated and irradiated material, from different processes. The curves shown are explained as follows. The decomposition of material which has been irradiated prior to decomposition has an induction period of 50 min (Curve *A*). Curve *B* represents the decomposition of unirradiated $KMnO_4$ interrupted at $t = 30$ min. The solid is then irradiated for the fixed time and the decomposition continued and completed. The acceleration due to "irradiation nuclei" should now occur at $t = (30 + 50)$ min if this acceleration is independent of the "thermal nuclei" operative in unirradiated material. The results verify this supposition. Similarly in the decompositions shown by curves *C*, *D*, and *E*, the

[10] D. B. BOWEN, R. R. EGGLESTON and R. H. KROPSCHOT, *J. Appl. Phys.* **23**, 630 (1952).
[11] N. F. MOTT, *Proc. Phys. Soc.* B **64**, 729 (1951).
F. SEITZ, *Advanc. Phys.* **1**, 43 (1952).
[12] J. S. KOEHLER, *Phys. Rev.* **60**, 397 (1941).
D. L. DEXTER, *Phys. Rev.* **86**, 770 (1952).
[13] R. S. PEASE, *Acta Cryst.* **7**, 663 (1954).
[14] P. M. HURLEY and H. W. FAIRBAIRN, *J. Appl. Phys.* **23**, 1408 (1952); *Bull. Geol. Soc. Amer.* **64** 659 (1953.)

times of divergence are found to be (50 + 45) min, (50 + 70) min, and (50 + 80) min respectively. In the case of runs *F* and *G* the times of interruption plus 50 min exceed the time of commencement of the decay period for an unirradiated specimen. The divergence from the unirradiated decomposition curve is absent and it is concluded that the accelerating effect of "irradiation nuclei" does not occur once the normal fracture of the crystal is completed.

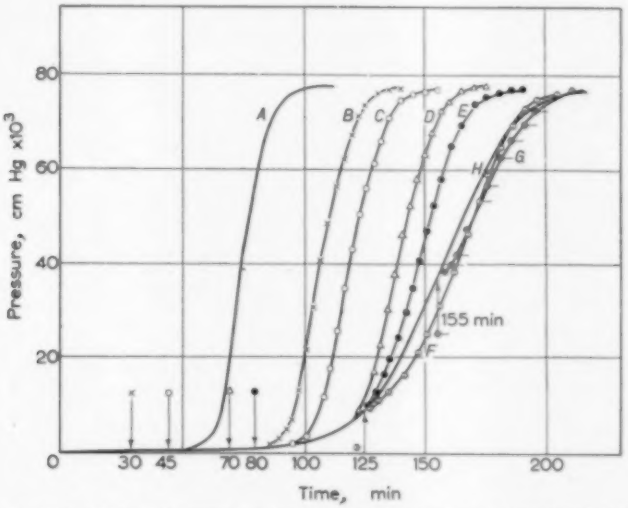

FIG. 8.—The effect of interrupting the decomposition of an unirradiated $KMnO_4$ crystal, irradiating in BEPO for 15 hr and continuing the decomposition with the original $t = 0$. The time of interruption in a particular case is shown by the appropriate arrow. The decomposition temperature was 215°C. Time of interruption:
$A = 0$; $B = 30$ min; $C = 45$ min; $D = 70$ min; $E = 80$ min; $F = 125$ min; $G = 155$ min; $H =$ no irradiation.

Failure to observe annealing of radiation effects at 70 ± 5°C above the irradiation temperature for 213 hr is in agreement with the observation that, in the case of graphite, appreciable annealing is found only at ~100°C above the exposure temperature.[15]

The various activation energies E_1, E_2, E_3, E_4 are close to the corresponding values for unirradiated material and it is therefore likely that the same chemical process is occurring. The fit of the PROUT–TOMKINS equation to the decay permits the use of the theory of decomposition already given.[1] Failure of the equation over the acceleration period in the case of large doses does not necessarily invalidate the previously proposed mechanism since over the short acceleration period the pressure is caused by preformed oxygen and the oxygen of decomposition. Fracturing of the crystal at the start of the acceleration period will create surfaces on which nuclear formation is favoured, and decomposition will proceed by propagation of the reaction along cracks.

Acknowledgement—This work was begun at Harwell where the author held a Senior Research Fellowship for which he wishes to thank the United Kingdom Atomic Energy Authority.

[15] W. K. WOODS, L. P. BUPP and J. F. FLETCHER, *Proceedings of International Conference on Peaceful Uses of Atomic Energy, Geneva*, 1955, Paper 746. United Nations (1956).

J. Inorg. Nucl. Chem., 1958, Vol. 7, pp. 378 to 383. Pergamon Press Ltd., London

THE PHOTOCHEMICAL REDUCTION AND THE AUTOREDUCTION OF NEPTUNIUM(VI)*

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(*Received* 11 *April* 1958)

Abstract—It was found that exposure of Np(VI) perchlorate solutions at 25° to 2537 Å light results in the formation of Np(V) with an apparent quantum yield of 0·032 ± 0·011. In addition the rate constant for the autoreduction of Np(VI) → Np(V), due to the radiolysis caused by the α-decay of ^{237}Np, was measured as $k = 3{\cdot}1 \pm 0{\cdot}2 \times 10^{-6}$ sec^{-1}. This result is discussed in comparison with the autoreduction rate constants of Pu(VI) and Am(VI).

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THE absorption spectra[1] of Np(VI) in perchloric acid media exhibits the beginning of an intense band starting at about 400 mμ. This ultra-violet absorption may be considered to be an electron transfer band,[2] or it may correspond to the fully permitted transition between the 5*f* and 6*d* levels of the cation.[3] This investigation was undertaken to determine if there is a photochemical reaction in conjunction with this absorption. In the course of the investigation evidence was obtained for the autoreduction of Np(VI) caused by the products of the α-particle irradiation of the solutions due to the decay of ^{237}Np.

EXPERIMENTAL

Stock solutions of Np(VI) in one molar perchloric acid were prepared by electrolytic oxidation. Aliquots of the stock solutions were then diluted with perchloric acid–sodium perchlorate solutions to maintain the ionic strength at unity. Gross neptunium concentrations were determined radiometrically. Np(V) concentrations were determined by measuring the 980 mμ absorption peak, either with a Beckman Model DU spectrophotometer or with a Cary Model 14 MR recording spectrophotometer. A calibration curve was used in conjunction with the Beckman spectrophotometer since with this instrument the 980 mμ band fails to conform to the Beer–Lambert law.[1]

Fig. 1 illustrates the experimental set up employed for the photochemical reduction. The combination of a General Electric 4W germicidal lamp with a Corning #9863 filter yields primarily the 2537 Å Hg line. The compound actinometer was similar to the design of LEIGHTON and FORBES[4] and consisted of four fused silica 1 cm cells. Cell 3 contained 2 ml of Np(VI) solution and cells 1, 2, and 4 each contained 2 ml of the actinometer solution—0·01 M uranyl oxalate† and 0·05 M oxalic acid.

Irradiations were usually carried out for 14 hr. At the half-way point cells 1,2 and 3,4 were interchanged to average out any differences in light intensity from the two

* Based on work performed under the auspices of the U.S. Atomic Energy Commission.
† Very pure uranyl oxalate was kindly supplied by J. L. WEEKS of this laboratory.

(1) R. SJOBLOM and J. C. HINDMAN, *J. Amer. Chem. Soc.* **73**, 1744 (1951).
(2) E. RABINOWITCH, *Rev. Mod. Phys.* **14**, 112 (1942).
(3) J. C. EISENSTEIN and M. H. L. PYRCE, *Proc. Roy. Soc.* A **229**, 20 (1955).
(4) W. G. LEIGHTON and G. S. FORBES, *J. Amer. Chem. Soc.* **52**, 3139 (1930).

paths. Continuous stirring was accomplished by bubbling nitrogen approximately saturated with water-vapour at room temerature through capillary fluorothene-tubing. All experiments were carried out in a constant temperature room, 25° ± 1°. To correct for volume changes due to evaporation (bubbling), a second gross neptunium assay was carried out at the end of the irradiation period. Generally about a 5 per cent increase in concentration was observed.

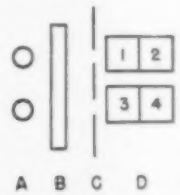

FIG. 1.—Schematic representation of photochemical reduction apparatus.
A—U-shaped germicidal lamp; *B*—Corning filter 9863; *C*—Mask with 5/16 in. dia. circular apertures; *D*—Compound actinometer.

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The amount of oxalate decomposed in each of the actinometer cells was determined by titration with ceric perchlorate to the ferroin end-point. All ceric solutions were standardized immediately prior to use, and the initial amount of oxalate was determined by titrating samples of the actinometer solution that had been kept in the dark. Titrations were carried out directly in the silica absorption cells by use of a 1 ml Gilmont Ultramicroburet. A precision of a few parts per thousand was readily obtained in these titrations.

Representing the number of moles transformed in the respective cells by m_1, m_2, m_3 and m_4, quantum yields were calculated by the following equation.[4]

$$\text{Quantum yield Np(V)} = \frac{0{\cdot}6m_3(m_1 - m_2)}{m_1(m_1 - m_4)} \tag{1}$$

The value 0·6 represents the quantum yield of the uranyl oxalate actinometer at 2537 Å.[4]

RESULTS AND DISCUSSION

Preliminary experiments indicated that a dark reaction of some type was occurring in the solutions of Np(VI) in perchloric acid. It was found that additional Np(V) was produced at a small but measureable rate after illumination with ultra-violet light had been discontinued. In order to demonstrate that something other than a photochemical after effect was involved, a series of solutions of varying perchloric acid and Np(VI) concentration were prepared; and the characteristic peak of Np(V) at 980 mμ was monitored. Constant ionic strength was not maintained in these experiments.

Assuming that the dissociation products of water formed by the α-particle irradiation reduce the Np(VI) to Np(V), we may write

$$d[\text{Np(V)}]/dt = k[\text{Np}] \tag{2}$$

where [Np] is the total neptunium concentration of the solution and k is the apparent rate constant for the autoreduction of Np(VI). Table 1 summarizes the results obtained. The data indicate that the apparent rate constant is adequately described by (2) and is independent of hydrogen ion concentration and ionic strength.

* All ± values in this paper are the statistical 95 per cent confidence limits.

From the mean value of $k = 3{\cdot}1 \pm 0{\cdot}2^* \times 10^{-9}$ sec^{-1}, the half-life of ^{237}Np ($2{\cdot}2 \times 10^6$ years) and the energy of its α- particles (4·8 MeV), one can calculate a value G[Np(V)] of 6·4 where G is the conventional radiation yield or molecules produced per 100 eV of absorbed energy. Implicit in the above calculation is the assumption that the γ-rays associated with the α-decay of ^{237}Np do not make a significant contribution to the radiolysis of the solutions.

From the value of the specific rate constant reported for the autoreduction of Pu(VI)[5] ($k = 1{\cdot}5 \times 10^{-7}$ sec^{-1}) and of Am(VI)[6] ($k = 1{\cdot}1 \times 10^{-5}$ sec^{-1}), using the

TABLE 1.—AUTOREDUCTION OF NEPTUNIUM(VI)

[Np] (mole/l.)	(H$^+$) (mole/l.)	d[Np(V)]/$dt \times 10^{10}$ (mole/l/sec)	$k \times 10^9$ (sec^{-1})
0·198	0·48	5·78	2·9
0·105	0·58	3·07	2·9
0·0437	0·79	1·44	3·3
0·298	1·00	8·63	2·9
0·304	1·00	8·86	2·9
0·105	1·53	3·23	3·1
0·119	1·70	4·04	3·4
0·130	1·70	4·03	3·1

respective values of the half-lives ($2{\cdot}4 \times 10^4$ years; 458 years) and α-energies (5·2 MeV; 5·5 MeV), and subject to the same assumption previously made, one may calculate a value of G[Pu(V)] = 3·2 and G[Am(V)] = 4·2.

The difference between these values cannot be due to the coincident γ-activity associated with the complex α-decay scheme of ^{237}Np since the total energy available from that source is much too small. The observed variances may be qualitatively understood, however, in terms of the following general mechanism.[7]

$$MO_2^{2+} + H = MO_2^{+} + H^{+} \quad (3)$$

$$MO_2^{2+} + H_2O_2 = MO_2^{+} + H^{+} + HO_2 \quad (4)$$

$$MO_2^{2+} + HO_2 = MO_2^{+} + H^{+} + O_2 \quad (5)$$

$$MO_2^{+} + OH = MO_2^{2+} + OH^{-} \quad (6)$$

$$MO_2^{2+} + Cl^{-} = MO_2^{+} + \tfrac{1}{2}Cl_2 \quad (7)$$

Since due to its longer half-life the concentration of neptunium was necessarily higher than that of the americium or plutonium, the probability is greater for the reaction of the neptunium with the primary products of water dissociation (the free radicals H and OH). It was pointed out by Dr. E. J. HART that if reactions (3) and (6) are important in producing the observed effect, experimental verification of this fact is feasible. Accordingly, a solution 0·1 M in Np(VI) and 1·1 M in perchloric acid was

[5] M. KASHA, *The Transuranium Elements, National Nuclear Energy Series* Vol. 14B, Paper 3.100, p. 326. McGraw-Hill, New York (1949).
[6] S. R. GUNN and B. B. CUNNINGHAM, *J. Amer. Chem. Soc.* **79**, 1563 (1957).
[7] A convenient summary of radiolysis theory and data is presented by E. J. HART, *J. Chem. Educ.* **34**, 586 (1957).

irradiated with a ^{60}Co γ-source. A value $G[Np(V)] = 3{\cdot}4$ was obtained. Assuming a mechanism for Np(V) formation similar to that of Ce^{+3}[7] and that there is no interference in the radiolysis yields of hydrogen and hydrogen peroxide, we can calculate a value from the data of COTTIN[8] of $G[Np(V)] = 4G(H_2O_2)\text{-}2G(H_2) = 2{\cdot}06$.

It should be noted that high values of $G[Np(V)]$ can readily be accounted for in the case of the α-irradiation of the solutions if reaction (3) is favoured over the combination of H radicals to form H_2. In addition the radiolysis of perchloric acid solutions yields chloride ion[8] which will reduce Np(VI)[9] and Am(VI)[10] but will very probably not reduce Pu(VI).

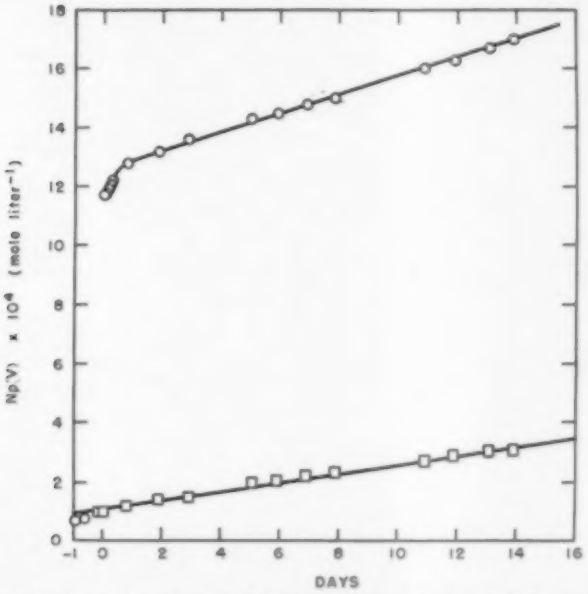

FIG. 2.—Photo and autoreduction of Np(VI). Circles are for sample before and after exposure to ultra-violet. Squares are for blank solution. Zero time corresponds to end of ultra-violet irradiation.

A detailed study of the reduction of Np(VI) by hydrogen peroxide is now being completed in this laboratory and when finished will add to our knowledge of the mechanism proposed.

In the photoreduction experiments duplicate samples of Np(VI) were prepared, one cell kept in the dark, the other sample irradiated with ultra-violet light and both samples analysed spectrophotometrically for the amount of Np(V) produced. The results of a typical run are depicted in Fig. 2. The lower curve is for the blank and illustrates the autoreduction while the upper curve shows the results obtained after exposing the sample to the mercury lamp for a 14 hr period.

Examination of this graph clearly indicates the existence of a pronounced photochemical aftereffect. For ca. the first 24 hr after the sample has been removed from the

[8] M. COTTIN, *J. Chem. Phys.* **53**, 903 (1956).
[9] J. C. HINDMAN, L. B. MAGNUSSON and T. J. LACHAPELLE, *The Transuranium Elements, National Nuclear Energy Series* Vol. 14B, Paper 15.2, p. 1039. McGraw-Hill, New York (1949).
[10] G. R. HALL and P. D. HERNIMAN, *J. Chem. Soc.* 2214 (1954).

ultra-violet source, a reduction reaction is occurring which has a different rate than the dark reaction. Photoactivated nitrogen was ruled out as a possible cause by using helium in one run for the stirring. A control experiment testing the perchloric acid was carried out by exposing a 1 M solution to ultra-violet and then adding Np(VI) after the irradiation. No increase in the autoreduction rate was observed.

Hydrogen peroxide in the amount that could be expected to be formed and present at the end of the irradiation was found to react completely within the time of mixing to produce a stoicheiometric amount of Np(V). The observed reaction is much too slow to be accounted for by the production of Np(IV) and its subsequent reaction with Np(VI),[11] and in addition no spectrophotometric evidence for the presence of Np(IV) was obtained even after a prolonged irradiation of a Np(VI) stock for 56 hr. There remains no readily apparent interpretation of the photochemical aftereffect.

TABLE 2.—PHOTOREDUCTION OF NEPTUNIUM (VI)

Initial Np(VI) (mole/l.)	Initial (H^+) (mole/l.)	$k \times 10^5$ (sec^{-1})	Quantum yield for Np(V)
0·0427 (A)	1·00	5·2	0·041
0·0423 (B)	0·87	7·8	0·032
0·0426 (B)	0·94	4·8	0·024
0·0437 (B)	0·79	5·2	0·031
0·0450 (C)	0·92	10·6	0·068
0·0424 (C)	0·22	10·6	0·061

(A), (B) and (C) represent runs made with three different preparations of Np(VI) stock solutions.

After exposure to ultra-violet all solutions were analysed periodically for a sufficient length of time to allow the linear tail of the curves to be well defined. Values of k, as defined by equation (2), were calculated for the irradiated samples. The apparent quantum yield of Np(V) was calculated in the manner previously described, using the Np(V) concentration determined immediately after the end of the irradiation. The data obtained are summarized in Table 2. Exposure time was 5·5 hr for the first entry and 14 hr for all other runs. The intensity of the light source was approximately the same for all experiments.

The marked increase in the k values listed above as compared to the results of Table 1 plus the variation of the quantum yields with the Np(VI) stock are considered to be reflections of the presence of photoactivated impurities in the stock solutions. On this basis the high quantum yields for the last two runs should probably be rejected. This results in a mean value of 0·032 $\pm$ 0·011 for the apparent quantum yield of Np(V).

A simplified representation of the observed photoreduction may be written as:

$$NpO_2^{2+}\cdot H_2O + h\nu = NpO_2^{+} + H^{+} + OH \qquad (8)$$

followed by reactions of the type previously presented in equations (4), (5) and (6).

The photoreduction of Np(VI) poses many interesting problems since both the initial reactant and product can be described, to a very good approximation,[3] as a

[11] J. C. HINDMAN, J. C. SULLIVAN and D. COHEN, *J. Amer. Chem. Soc.* **76**, 3278 (1954).

linear molecule O—Np—O with the additional electron (Np VI) or electrons (Np V) moving in the field of the central core and with only minor interactions with their co-ordination sphere of water molecules. However, with the present amount of information available it is not profitable to elaborate on detailed possible mechanisms.

Acknowledgements—It is a pleasure to extend our appreciation for several helpful discussions with Dr. E. J. HART of this laboratory. In addition he arranged for the ^{60}Co irradiation experiment during which Miss P. WALSH provided valuable technical assistance.

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KINETICS OF THE REDUCTION OF U_4O_9 IN HYDROGEN

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Abstract—The reduction of U_4O_9 powders in hydrogen was studied at temperatures of 400–600°C and at hydrogen pressures of 20–500 mm Hg. Under these conditions U_4O_9 is reduced to $UO_{2\cdot02\pm0\cdot02}$. X-ray diffraction studies showed that during reduction U_4O_9 is converted into the fluorite structure of uranium dioxide. X-ray data on U_4O_9 samples reduced at 470°C indicate that the initial reduction product is non-stoicheiometric UO_{2+x} ($0\cdot10 > x > 0\cdot06$). The rate data were analysed on the assumption that the reaction rate is controlled at the solid–gas interface, i.e., the particle surface. Rate constants and activation energies were calculated. The rate constant k fits an empirical expression of the form $k = Kf(p)e^{-E/RT}$, where E is the activation energy, $f(p)$ is an undetermined function of pressure and K is a proportionality constant. The term $f(p)$ is approximately equal to $p^{0\cdot7}$; however, the pressure dependence decreases with increasing pressure. A possible mechanism for the surface reaction is discussed. The calculated activation energy for the reduction of U_4O_9 is 25 ± 3 kcal/mole.

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IN the composition range UO_2–$UO_{2\cdot25}$ of the uranium–oxygen system, two thermodynamically stable phases exist, uranium dioxide and U_4O_9. GRONVOLD has shown that oxygen is soluble in the uranium dioxide lattice at high temperatures.[1] According to GRONVOLD, the boundary of the uranium dioxide phase increases from about $UO_{2\cdot03}$ at 400°C to about $UO_{2\cdot20}$ at 1000°C. The U_4O_9 phase has a relatively narrow range of non-stoicheiometric stability at these temperatures.

The uranium lattices in UO_2 and U_4O_9 are similar. UO_2 has a fluorite structure with a lattice parameter of 5·470 Å for the unit cell (U_4O_8). The nature of the oxygen lattice in U_4O_9 has not been established. The lattice parameter of the unit cell (U_4O_9), on the assumption that the structure is cubic, is 5·440 Å.

Several workers have studied the oxidation of UO_2 in air and oxygen.[2,3] At temperatures of 100–350°C, UO_2 is oxidized to a tetragonal phase, U_3O_7, or, under some conditions, to U_4O_9. At temperatures above 250°C, U_3O_7 is oxidized in a second step to U_3O_8. The rate of oxidation of UO_2 to U_3O_7 or U_4O_9 is controlled by the diffusion of oxygen through the oxide lattice. Oxidation of U_3O_7 to U_3O_8 is autocatalytic, indicative of a nucleation and growth process.

The present work is a kinetic study of the reduction of U_4O_9 powder by gaseous hydrogen. The reduction was studied at temperatures of 400–600°C and at pressures of 20–500 mm Hg.

EXPERIMENTAL

Apparatus

The recording vacuum balance, X-ray and surface area equipment used in this study have already been described in connexion with the kinetic study of the oxidation of UO_2.[3]

[1] F. GRONVOLD, *J. Inorg. Nucl. Chem.* **1**, 357 (1955).
[2] J. S. ANDERSON, L. E. J. ROBERTS and E. A. HARPER, *J. Chem. Soc.* 3946 (1955).
[3] S. ARONSON, R. B. ROOF and J. BELLE, *J. Chem. Phys.* **27**, 137 (1957).

Procedure

Before each run, the U_4O_9 sample (weighing approximately 0·5 g) was evacuated to pressures of 10^{-2} to 10^{-3} mm and was flushed several times with helium. It was then heated to the reaction temperature in 300 mm of helium gas. The system was evacuated to 10^{-2} mm and hydrogen gas was admitted. The use of helium essentially eliminated the slow oxidation of the sample which occurred on heating *in vacuo* (10^{-2}–10^{-3} mm). Pressures up to 400 mm were measured by a Wallace and Tiernan absolute pressure manometer; a mercury manometer was used for the measurement of higher pressures. The compressed hydrogen was purified by passing it over palladized asbestos at 400°C and then over magnesium perchlorate. The compressed helium was dried over magnesium perchlorate.

Materials

Three U_4O_9 powders were used in this study. Two of the powders were prepared from the same uranium dioxide source. The uranium dioxide was prepared from UO_3 obtained by pyrolysis of Mallinckrodt Chemical Works uranyl nitrate hexahydrate at 300°C. The UO_3 was ball-milled and reduced to UO_2 by heating in hydrogen at 500°C. The two U_4O_9 powders were prepared by controlled oxidation of this UO_2 preparation to $UO_{2\cdot25}$ in oxygen at temperatures below 200°C. One of these powders, designated as powder A, was annealed *in vacuo* at 800°C for 1 week. The second powder, designated as powder B, was annealed *in vacuo* at 200°C for 3 weeks. A third U_4O_9 powder, designated as powder C, was prepared from uranium dioxide that was obtained from the Mallinckrodt Chemical Works. The MCW UO_2 was oxidized to $UO_{2\cdot25}$ in the manner indicated above and was annealed at 800°C for 1 week.

The surface areas of powders A and B were 0·73 m^2/g and 1·75 m^2/g, respectively, whereas that of the uranium dioxide powder from which they were prepared was 2·4 m^2/g. The surface areas of powder C and the MCW UO_2 powder were 0·45 m^2/g and 0·54 m^2/g respectively. The annealing process thus caused a reduction in surface area, especially in the case of powder A. X-ray diffraction patterns and chemical analyses of the three powders showed that they were U_4O_9.

The compositions of the oxide samples calculated from the weight changes during reduction were checked on some samples by chemical analyses. The O/U ratio calculated by the two methods agreed to $\pm$0·01.

RESULTS AND DISCUSSION

Typical rate curves for the reduction of the three U_4O_9 powders in hydrogen at constant pressure and temperature are shown in Fig. 1. The forms of the rate curves obtained for the three powders were fairly similar over the range of temperatures and pressures studied. However, the rate curves obtained with powder B were generally more nearly linear than those obtained with the other two powders. Weight changes on the samples indicated that the reduction product was $UO_{2\cdot02\pm0\cdot02}$. The limits of $\pm$0·02 on the composition of the reduced samples refer to the possible experimental error in determining the composition from the weight change. No consistent variation of composition with temperature or pressure was observed.

Surface area measurements were made on samples of powders A and C reduced at 410°C. The values obtained on the two reduced samples were 0·80 m^2/g and 0·45 m^2/g, respectively. Thus, little particle breakdown occurred during reduction.

X-ray diffraction powder patterns were taken at room temperature of samples of powders A and C that were partially reduced at 470°C. Similar results were obtained on both powders. A mixture of U_4O_9 and UO_{2+x} was observed on partially reduced samples of compositions above $UO_{2\cdot10}$. The subscript x, the value of which is less than 0·10, is used to indicate the possibility that the uranium dioxide phase is not

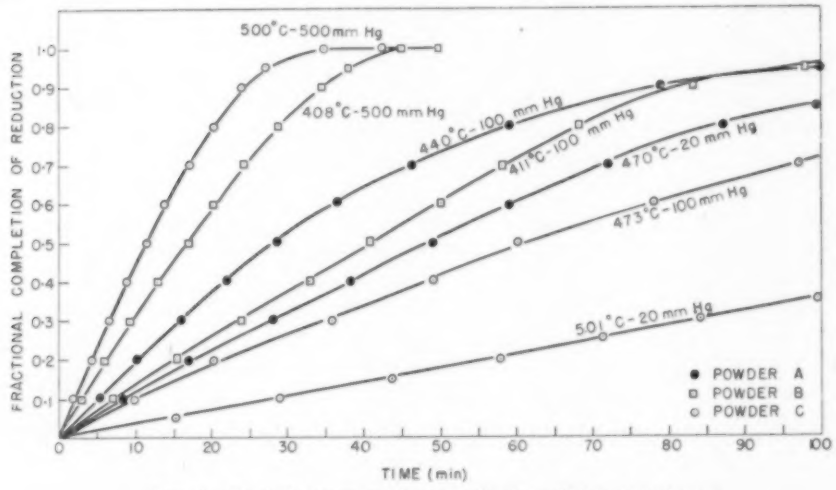

FIG. 1.—Typical rate curves for the reduction of U_4O_9 in hydrogen.

stoicheiometric. The relative amount of the UO_{2+x} phase increased with the degree of reduction. The U_4O_9 phase was not detected in samples of composition below $UO_{2\cdot10}$. It thus appears that the reduction process initially converts U_4O_9 into non-stoicheiometric UO_{2+x} ($0\cdot10 > x > 0\cdot06$). The oxygen content of the latter phase is then reduced until a composition of $UO_{2\cdot02\pm0\cdot02}$ is attained. The wide limits for the value of x in the initial reduction product are given to take into account the possibility that the presence of 10–15 per cent of the U_4O_9 phase may be required for its appearance in the X-ray patterns. The X-ray data are in qualitative agreement with the limit of about $UO_{2\cdot06}$ for the boundary of the UO_{2+x} phase at 470°C given by GRONVOLD.[1]

For the kinetic interpretation of the data, it will be assumed that penetration of the UO_2 lattice by hydrogen is not an important consideration. The work of ROBERTS[4] on the chemisorption of hydrogen on UO_2 indicates that some absorption into the lattice may occur; the rates of absorption appear to be low however.

A reasonable reduction mechanism comprising three processes can be postulated for the reduction of U_4O_9; (1) the reaction between hydrogen and lattice oxygen at the particle surface with the formation of water; (2) the transformation of U_4O_9 to UO_{2+x} at the interface between the phases; and (3) the diffusion of oxygen, released at this interface, through the UO_{2+x} phase to the solid–gas interface, i.e. the particle surface. For simplicity, the possible non-stoicheiometry of the product phase is temporarily neglected.

The form of the rate curves indicates that the diffusion process is not rate controlling. The rate curves are not parabolic in form. In agreement with this conclusion

[4] L. E. J. ROBERTS, *J. Chem. Soc.* 3939 (1955).

are the data from the study of the oxidation of UO_2[2,3] that predict a very rapid rate of diffusion of oxygen in the UO_{2+x} phase at temperatures above 400°C.

The equation that would be applicable if the interface reaction, the conversion of U_4O_9 to UO_{2+x} were rate controlling is, in the case of uniform spherical particles,[5]

$$(1 - c)^{1/3} = 1 - (k_1 t/r_0) \quad (1)$$

where c is the fractional weight loss at time t with values from 0 to 1, k_1 is the rate constant, and r_0 is the particle radius.

If reaction at the particle surface is rate controlling, since the surface area and gas pressure remain constant, the simplest mechanism would give a constant reaction rate in the case of a powder of uniform particle size. A simple rate equation can be written in this case:

$$c = k_2 t/r_0 \quad (2)$$

The forms of the rate curves obtained with the three powders were intermediate between the theoretical curves predicted by equations (1) and (2). It is difficult to determine from the form of the experimental rate curves which mechanism is more applicable. Other evidence, however, indicates that the surface reaction is of primary importance in the reduction kinetics. The reaction rate was found to vary with the 0·5–0·9 power of the hydrogen pressure, as is discussed below. It is difficult to reconcile this relatively strong pressure dependence with a mechanism in which the rate controlling step is the conversion of U_4O_9 to UO_{2+x} at the phase interface. Also, the relatively large degree of non-stoicheiometry of the initial reduction product, indicated by the X-ray measurements, can probably best be explained on the assumption that the surface reaction is slow compared with the kinetic processes in the solid. The process of homogenization within the solid would result in a high concentration of non-stoicheiometric oxygen in the uranium dioxide phase. The uranium dioxide fluorite structure is capable of absorbing a relatively large concentration of oxygen presumably into interstitial sites in the lattice.[1,2]

For the quantitative treatment of the data, it was assumed that the mechanism corresponding to equation (2) is applicable. Possible reasons for the deviations from linearity of the rate curves are discussed below. Rate constants were determined for the initial slopes of the plots of weight loss versus time. The plots were fairly linear up to c values of 0·7–0·8 for powder B and up to c values of 0·4–0·6 for powders A and C. Rate constants were calculated in terms of the number of moles of oxygen released per square centimetre of surface per second. The surface area values given previously were used.

Plots of log k versus $1/T$ at hydrogen pressures of 20, 100 and 500 mm are given in Figs. 2–4 and the activation energies calculated by least-squares analyses are listed in Table 1. Figs. 2–4 also give some indication of the dependence of reaction rate on hydrogen pressure. Reaction rates at two additional pressures were determined for powders A and C at temperatures of 470°C and 500°C, respectively. The variation of the rate constant with pressure is shown in Fig. 5. The dependence of reaction rate on hydrogen pressure was calculated from least-squares plots to be approximately 0·7. However, the pressure dependence of the reaction rate decreases with increasing pressure.

[5] P. W. M. JACOBS and F. C. TOMPKINS, *Chemistry of the Solid State* (Edited by W. E. GARNER) Chap. 7. Butterworths, London (1955).

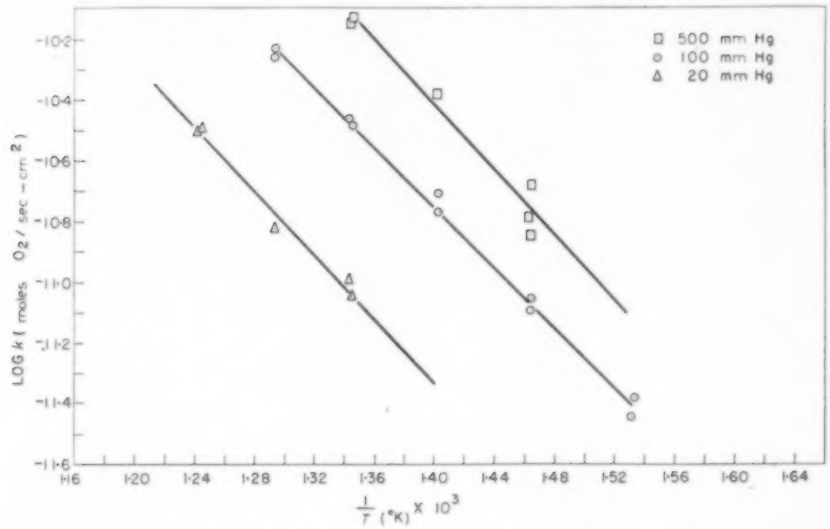

FIG. 2.—Rate constant as a function of temperature for powder A.

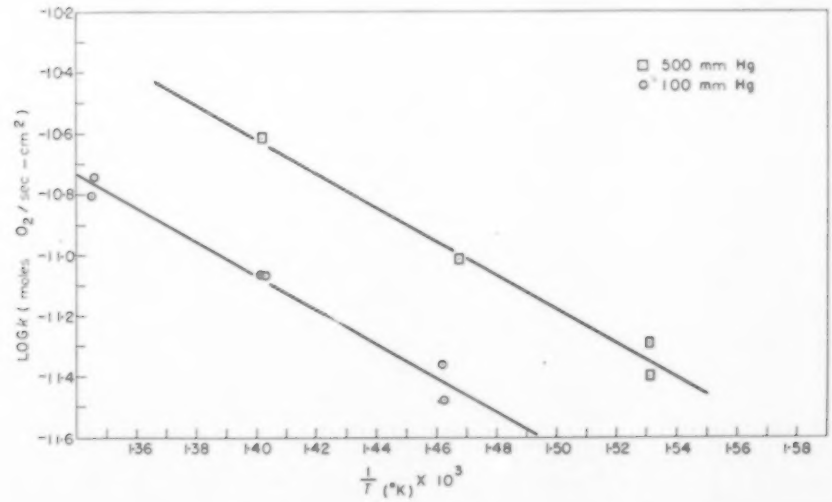

FIG. 3.—Rate constant as a function of temperature for powder B.

The rate constants approximately fit an equation of the form $k(T, p) = Kf(p)e^{-E/RT}$, where $f(p)$ is an undetermined function of pressure and is approximately equal to $p^{0.7}$, E is the activation energy and K is a proportionality constant.

The reaction at the surface, although possibly occurring at a constant rate, may be quite complex. It probably involves the adsorption and possibly the decomposition of hydrogen molecules into atoms on the solid surface, the reaction of these hydrogen atoms with lattice oxygen and the desorption of water from the solid.

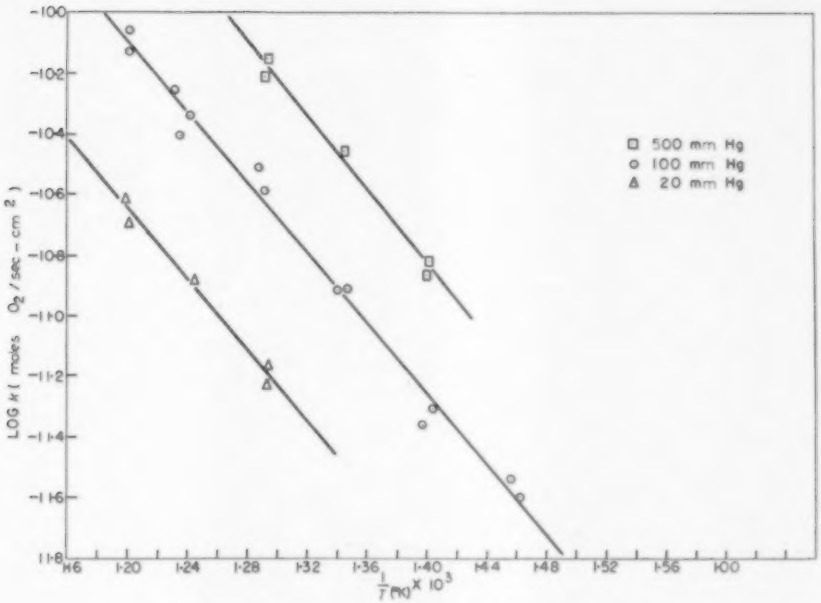

FIG. 4.—Rate constant as a function of temperature for powder C.

TABLE 1.—CALCULATED ACTIVATION ENERGIES FOR THE REDUCTION OF U_4O_9 TO UO_2

Powder type	Hydrogen pressure (mm Hg)	Activation energy (kcal/mole)
A	20	24·4
A	100	22·6
A	500	24·9
B	100	25·6
B	500	25·6
C	20	26·7
C	100	26·6
C	500	28·1

A reasonable reaction scheme for the reduction process can be qualitatively formulated as follows:

$$H_2\ (gas) \underset{k-1}{\overset{k1}{\rightleftharpoons}} 2H(a) \tag{3}$$

$$H\ (a) + O(l) \underset{k-2}{\overset{k2}{\rightleftharpoons}} O{-}H^* \tag{4}$$

$$O{-}H^* + H(a) \xrightarrow{k3} H_2O(a) \tag{5}$$

$$H_2O(a) \xrightarrow{k4} H_2O\ (gas) \tag{6}$$

The symbol a represents the adsorbed state, $O(l)$ represents lattice oxygen ions in excess of the composition UO_2 at the particle surface and O–H* represents an oxygen–hydrogen complex of unknown stability.

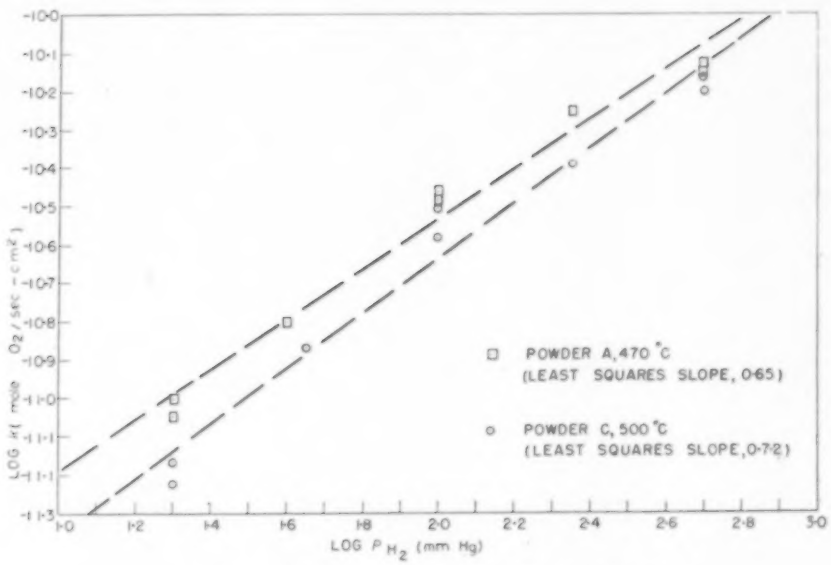

FIG. 5.—Rate constant as a function of hydrogen pressure.

The assumption that hydrogen decomposes into atoms on the surface of the solid, expressed in equation (3), is suggested by the fact that the dependence of the reduction rate on pressure is a fractional power less than one and that the dependence approaches 0·5 at the higher pressures. This fractional dependence is most easily accounted for by assuming hydrogen decomposition. Using the proper assumptions and including at least one of the inverse reaction steps in the mechanism, it is possible to derive rate equations which are in reasonable agreement with the data. Quantitative interpretation will not be attempted, however, since the proposed mechanism requires further substantiation. The above discussion does point up the fact that the reduction of U_4O_9, like many surface reactions, is complex and the rate is probably controlled by more than one elementary process. The experimental activation energy is probably a composite activation energy involving more than one reaction step. Considering the probable complexity of the reaction, it is interesting that the temperature dependence of the reduction rate is experimentally independent of pressure.

It has been assumed in the discussion that the reaction rate is controlled by a surface reaction occurring at a constant rate. The experimental rate curves, however, deviate considerably from linearity in the latter stages of the reaction. A reason for this deviation is that the real powders are not composed of uniform spherical particles as assumed but are distributed in size and shape. The smaller particles are consumed earlier in the reaction causing a decrease in the surface area effective in the reduction. The gradually decreasing surface area leads to a gradually decreasing reaction rate. Another possible reason for the decreasing reaction rate is the fact that a non-stoicheiometric product is initially formed on reduction. The rate of reduction may be controlled at least partially by the rate of abstraction of oxygen from the solid. After the U_4O_9 phase is entirely consumed, the concentration of oxygen in UO_{2+x} would decrease gradually, possibly causing a decrease in reaction rate. Another

possibility, which appears less likely however, is that an accumulation of adsorbed water formed on reduction impedes the reaction.

If the reduction rates were purely characteristic of the chemical nature of the solid, the calculated rate constants and activation energies would be independent of the type of U_4O_9 powder used. The differences in these values among the three powders probably are due to differences in the nature of the solid surfaces. The variability of solid surfaces is a well known phenomenon.

Acknowledgements—This work was performed under contract AT-11-1-GEN-14. The authors are grateful to the U.S. Atomic Energy Commission and the Westinghouse Electric Corporation for permission to publish this paper.

The authors wish to acknowledge the very able assistance of R. T. Parks in carrying out the experimental work and wish to thank Dr. R. B. Roof, Jr. for his help in interpreting the X-ray patterns. The authors also wish to acknowledge the helpful discussion of this work with Dr. J. Belle.

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OXYGEN EXCHANGE BETWEEN URANIUM OXIDES AND WATER*

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Abstract—The exchange of ^{18}O between liquid water and various uranium oxides has been studied at temperatures up to the critical temperature of water. Uranium dioxide and U_3O_8 undergo oxygen exchange only at elevated temperatures, whereas uranium trioxide is found to exchange oxygen with liquid water to a readily measurable extent even at 25°C; in the latter case exchange is complete in 4 hr at 100°C.

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SEVERAL reactions involving the exchange of oxygen between solid oxides and oxygen gas have been reported in the recent literature.[1–4] Most of these studies were aimed at a correlation of the exchangeability with catalytic efficiency of the oxide. In general the results were characterized by the occurrence of a rapid initial exchange involving only a few per cent of the total oxygen of the oxide followed by a very much slower reaction. This was interpreted as due to the exchange of the surface atoms of the oxide followed by: (a) a slower exchange of less "active" surface atoms, or (b) a rate limiting slow diffusion of atoms from within the crystal to the surface. Surface areas calculated for the oxides on the basis of assumption (b) agreed quite well with those obtained from nitrogen adsorption isotherms.

Previous studies involving the exchange of oxygen between oxides and water which we have seen reported are that by WHALLEY and WINTER[5] on the systems $H_2O_{(g)}$ and Al_2O_3, ThO_2 and TiO_2, that by CAMERON *et al.*[6] on $H_2O_{(g)}$ and V_2O_5, and that by HUTCHISON[7] on $H_2O_{(g)}$ and SiO_2. A behaviour similar to that found for the oxide–O_2 systems was observed, i.e., a relatively fast reaction of a small fraction of the total oxide followed by a very much slower exchange. The initial exchange, partially with residual water was observed as low as 20°C with Al_2O_3 and 120°C with ThO_2 and TiO_2. With Al_2O_3, the slow exchange was not measurable until 200°C.

We have studied, as a part of a geochemical investigation,[8] the exchange of oxygen between water and various uranium oxides. Reaction was found to be measurable within a few hours at 300°C for UO_2, 350°C for U_3O_8 and very rapid with UO_3

*Based on work performed under the auspices of the U.S. Atomic Energy Commission.

[1] N. MORITA, *Bull. Chem. Soc. Japan* **15**, 1 (1940).
[2] G. HOUGHTON and E. R. S. WINTER, *Nature, Lond.* **164**, 1130 (1949).
[3] J. A. ALLEN and I. LAUDER, *Nature, Lond.* **164**, 142 (1949).
[4] E. R. S. WINTER, *J. Chem. Soc.* 1170 (1950).
[5] E. WHALLEY and E. R. S. WINTER, *J. Chem. Soc.* 1175 (1950).
[6] W. C. CAMERON, A. FARKAS and L. M. LITZ, *J. Phys. Chem.* **57**, 229 (1953).
[7] D. A. HUTCHISON, *J. Chem. Phys.* **22**, 758 (1954).
[8] H. R. HOEKSTRA and J. J. KATZ, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1955, Vol. 6, p. 547. United Nations (1956).

at 100°C. A dependence of the exchangeability on the method of preparation of the oxide was observed.

EXPERIMENTAL

Reactant materials

$H_2{}^{18}O$ containing 0·011 mole fraction ^{18}O ($N_{^{18}O}$) was used in these experiments. It was purified by triple distillation successively from alkaline permanganate and acid dichromate solutions, followed each time by passage through a silica tube at 800°C. In all experiments water was heated just before use and had a pH near 6·5.

The UO_2 used was a commercial product prepared by a high temperature reduction of a higher oxide. Oxides from two different sources were used, one corresponding to the formula $UO_{2.08}$ and the second to $UO_{2.04}$ (determined by ignition to U_3O_8). These are referred to as source no. 1 and no. 2 respectively. X-ray analysis of the material from source no. 1 revealed a very well defined pattern characteristic of UO_2. UO_2 enriched in ^{18}O was prepared by direct exchange of these oxides with $H_2{}^{18}O$ at 380–400°C. At these temperatures complete equilibration was achieved within 24 hr. Following the exchange, the tagged oxide was dried *in vacuo* over P_2O_5. X-ray analysis of the oxide after complete equilibration with H_2O at 380°C revealed a pattern identical to that of the starting material.

The U_3O_8 oxide had been prepared by the ignition of spectroscopically pure uranyl nitrate. U_3O_8 enriched in ^{18}O was prepared by equilibration of this material with $H_2{}^{18}O$ at 380–400°C. X-ray analysis of the U_3O_8 before and after the equilibration with H_2O revealed no changes but a somewhat greater degree of disorder was observed to exist indicative of the formation of new chemical species in the crystals after the exchange.

The UO_3 used had been prepared by SHEFT *et al.*[9] by the reaction of O_2 with U_3O_8 at 600°C. X-ray analysis showed this material to be a finely divided crystalline product of the type known as "Mallinckrodt oxide".

Technical procedure

Weighed quantities of oxide and H_2O were introduced into an Inconel metal reaction tube of 9·6 cc volume. The tube was flushed out with nitrogen, sealed and introduced into a calibrated, sand-insulated furnace. Following an experiment, the water was removed and equilibrated with CO_2. After shaking for at least 16 hr the CO_2 was separated from the H_2O and analysed in the mass spectrometer for the ratio

$$R = C^{16}O_2/C^{16}O^{18}O.$$

The quantities of H_2O and CO_2 used for equilibration were such that any dilution of the ^{18}O in the H_2O by the CO_2 was well within the experimental error and no corrections were made for this effect. The mole fraction of ^{18}O in the water, $N_{^{18}O}$, was therefore calculated from the expression $N_{^{18}O} = 1/(KR + 1)$ where K, the equilibrium constant for the $C^{16}O_2$–$H_2{}^{18}O$ reaction, was assumed equal to 2·00.

In the oxide-water exchanges the equilibrium values for the mole fraction of ^{18}O in the water were calculated assuming a random distribution of the isotopes between the oxide and water.

Mass spectrometer

The mass spectrometer* employed in this work was designed by and constructed under the direction of one of us (D. A. H.). It was 60-degree sector-type direction-focussing instrument with a typical electron-bombardment type ion source, all metal tube construction, and a vibrating-reed electrometer for ion current detection.

RESULTS AND DISCUSSION

In Table 1 are summarized the results of several exchange experiments with the uranium oxides. It must be emphasized that these results are preliminary and the

* Description of instrument to be published elsewhere.

[9] I. SHEFT, S. FRIED and N. DAVIDSON, *J. Amer. Chem. Soc.* 72, 2172 (1950).

TABLE 1.—EXCHANGE REACTIONS OF URANIUM OXIDES

Oxide	Wt. of oxide (g)	Wt. of water (g)	Temp. (°C)	Time (hr)	F (%)
(1) UO_3	2·370	1·004	25	24	23·6
UO_3	2·370	1·004	100	4·4	100
(2) UO_2*	3·120	1·040	290	16	29·8
(2) UO_2*	3·120	1·040	350	3·0	36·7
(2) UO_2*	3·120	1·040	400	3·0	73·2
(3) U_3O_8	2·998	1·934	360	2·0	38·1
U_3O_8	7·186	4·000	360	2·0	57·3

* UO_2 from source No. 1.

conclusions tentative; more detailed investigation will be required before the exchange mechanisms can be formulated with confidence. A rather surprising result was the ready exchangeability of UO_3, with which reaction was detectable at 25°C and complete within 4 hr at 100°C. This exchange evidently proceeds by a mechanism involving hydrate formation for the UO_3 initially was orange, essentially anhydrous solid; as the reaction occurs, however, it takes on a brilliant yellow colour characteristic of UO_3 hydrates. X-ray analysis revealed the material after complete exchange at 100°C to be the monohydrate $UO_3 \cdot H_2O$.

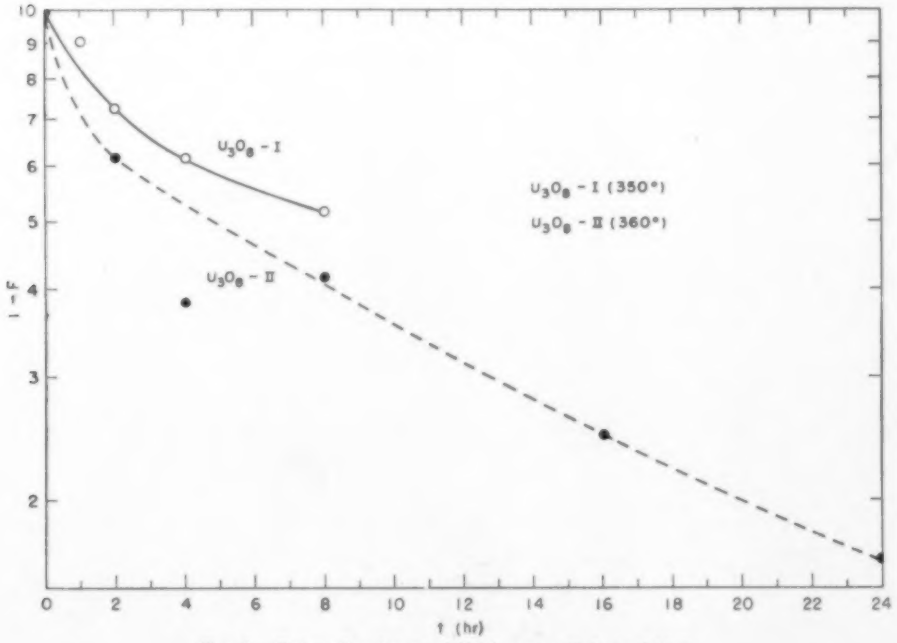

FIG. 1.—Rates of exchange of ^{18}O between U_3O_8 and H_2O.

In the reaction of H_2O with UO_2 and U_3O_8 both of which exchanged quite readily in the neighbourhood of 350°C, no evidence of stable hydrate formation was obtained. X-ray analyses of these oxides before and after equilibration with H_2O revealed no detectable chemical change.

A qualitative study of the rates of the exchange of UO_2 and U_3O_8 was made by preparing nearly identical samples of oxide and water (for a given series) and heating them in the reaction tube for varying intervals of time. The fractional exchange (F)

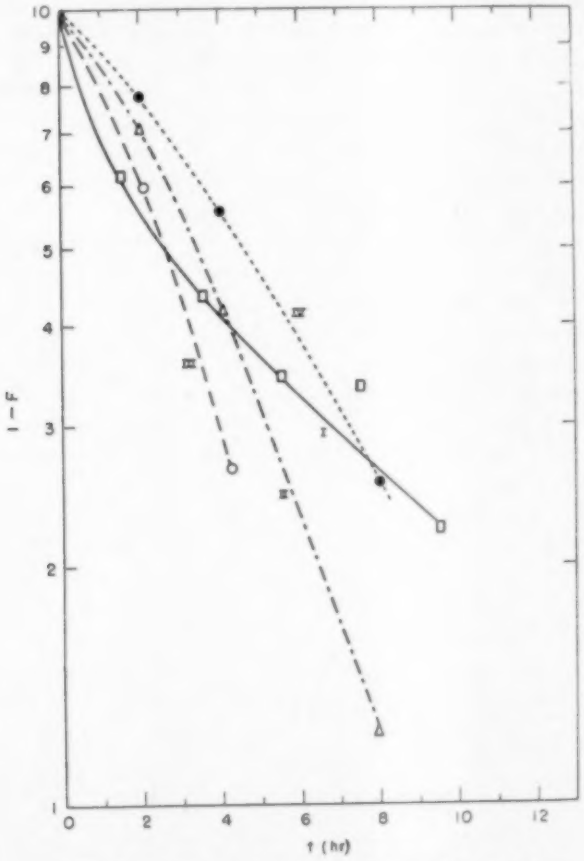

FIG. 2.—Rates of exchange of ^{18}O between UO_2 and H_2O.

I. 1·002 g UO_2 source no. 1; 1·000 g H_2O, 360° $(N_{18O})eq = 0{\cdot}002831$
II. 1·400 g UO_2 source no. 1; 1·934 g H_2O, 350° $(N_{18O})eq = 0{\cdot}002642$
III. 1·465 g UO_2 source no. 2; 1·934 g H_2O, 350° $(N_{18O})eq = 0{\cdot}002415$
IV. 1·465 g UO_2 source no. 2; 1·934 g H_2O, 317° $(N_{18O})eq = 0{\cdot}002415$

of the oxygen in the oxide was then determined on the basis of the calculated equilibrium mole fraction ^{18}O in the H_2O. Semilogarithmic plots of $(1-F)$ vs. time for two U_3O_8 series are shown in Fig. 1 (an induction period of 0·5 hr at 350°C was assumed to result from the time required for the tube and reactants to reach the temperature of the furnace). The observed variation of the rates with time is that expected for such a heterogeneous exchange reaction, i.e., an initial rapid reaction followed by a

progressively slower reaction rate as diffusion processes become important as rate-limiting steps. In contrast to the results on the systems studied by WINTER *et al.*, however, the rate of the slow exchange is seen to be of the same order of magnitude as that of the initial reaction and to go essentially to completion. This suggests that either (a) there is a relatively rapid diffusion of atoms from within a U_3O_8 particle to the surface or (b) an appreciable solution-recrystallization process occurs through which the oxide surface is constantly renewed and possibly undergoes a change in area. Evidence in favour of (b) is found in the corresponding rate curves for the exchange between H_2O and UO_2. In series II, III and IV (Fig. 2) an actual *increase* in the rate with time occurred. Because there was no chemical change, this is consistent with a process in which the net result is a breaking down of the oxide particles, with a resulting increase in the number of atoms available for exchange. Calculations based upon the vapour-pressure of H_2O at 350°C showed that in these series sufficient liquid was present during the exposure to completely cover the solid. Curve I shows the effect on the rate of decreasing the amount of H_2O and increasing the temperature toward the critical region. It is seen that although the initial exchange is more rapid than at 350°C the rate does fall off with time as in the U_3O_8 series. These results indicate that the presence or absence of a liquid phase is the factor which is responsible for this particular variation of the rate with time. A comparison of series I, Fig. 1 for U_3O_8 with series II and III, Fig. 2 for UO_2 in which comparable quantities of reactants were used at 350°C implies that the equilibrium $(U_3O_8)_S \rightleftharpoons (U_3O_8)_{aq}$. is attained considerably more slowly than that of the analogous reaction for UO_2.

The observed difference in the rates of the UO_2 exchange for oxide from different sources (Series II and III) is possibly due to a difference in the initial particle size.

Temperature coefficients calculated for the UO_2 exchange from the experiment at 290° and 350°, Table 1 (in which comparable fractions of exchange were attained) and from the half-times of series III and IV (Fig. 2) at 350° and 317° corresponded to activation energies of 23 and 13 kcal/mole. Calculation of these energies may not be justified due to the non-linear nature of the curves of Fig. 2.

Acknowledgements—We are indebted to DR. S. SIEGEL for performing the X-ray analyses on the uranium oxides, and to MR. L. G. POBO for mass spectrometric analyses.

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PROPERTIES OF SF_4 AND ITS ADDUCT WITH BF_3

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Abstract—Some new data on the adduct of SF_4 with BF_3 are reported and arguments are given, based on these and other data, to indicate that the adduct is quite unlikely to be a donor-acceptor complex. Infra-red examination proved inconclusive due to the instability and reactivity of the adduct. SF_4 has been found to react with F_2 producing SF_6 but is unreactive toward BrF_3 and Cl_2. It reacts rapidly with BCl_3 producing BF_3, SCl_2 and Cl_2 when in excess.

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WHILE the formation of sulphur tetrafluoride had been reported by a number of workers, only a few attempted to characterize the compound chemically and physically; its properties and even, by some authors, its existence, were considered uncertain until the definitive study of BROWN and ROBINSON.[1] These authors described a tedious but reliable method of preparation of the pure material and measured a number of its physical properties. Shortly thereafter, a study of the infra-red and Raman spectra[2] led to the conclusion that the molecule possesses C_{2v} symmetry. DODD *et al.*[2] further commented that this is the symmetry of the general structure to be expected by analogy with other halides of group V, VI and VII elements. In this case the structure may be considered to be derived from a trigonal-bipyramidal disposition of five pairs of valence shell electrons in a $3s3p^33d$ set of orbitals around the sulphur atom. By assuming one of the equatorial pairs of electrons to be the unshared pair, a structure of C_{2v} symmetry is obtained from this formalism. Strong and independent evidence for this structure has been obtained from studies of the fluorine nuclear resonance spectrum.[3] These nuclear resonance studies are completely conclusive in eliminating any higher symmetry (e.g. T_d, D_{4h}, C_{3v}) and very strongly, although not with absolute rigor, support the kind of C_{2v} structure described above.

In succeeding notes, BARTLETT and ROBINSON[4] reported observations on the formation by SF_4 of adducts with BF_3, AsF_5 and SbF_5 and also reported that compounds of analogous stoicheiometry are formed by SeF_4. It has further been stated by BARTLETT and ROBINSON[4a] that "there is evidence from electrical conductivity that SeF_4 ionizes to SeF_3^+ and SeF_5^- but very little that a similar fluorine transfer takes place in SF_4." They also advanced the tentative hypothesis that the SF_4 adducts with BF_3, AsF_5 and SbF_5 are simple donor-acceptor compounds while allowing that the compounds of SeF_4 having similar stoicheiometry might be ionic, e.g. $[SeF_3^+BF_4^-]$, etc.

In this communication some chemical and physical evidence bearing on the constitution of the adduct of SF_4 with BF_3 is presented and discussed. Other observations on the reactivity of SF_4 are also reported.

[1] F. BROWN and P. L. ROBINSON, *J. Chem. Soc.* 3147 (1955).
[2] R. E. DODD, L. A. WOODWARD and H. L. ROBERTS, *Trans. Faraday Soc.* **52**, 1052 (1956).
[3] F. A. COTTON, J. W. GEORGE and J. S. WAUGH, *J. Chem. Phys.* **28**, 994 (1958).
[4a] N. BARTLETT and P. L. ROBINSON, *Chem. & Ind.* 1351 (1956); [b] *Proc. Chem. Soc.* 230 (1957).

DISCUSSION

The constitution of the SF_4–BF_3 *adduct.** Certain of the data and observations reported in this communication as well as those previously given by ROBINSON *et al.* will be considered in regard to their bearing on the constitution of the SF_4–BF_3 adduct. Only the two extreme cases, viz. a simple Lewis acid–Lewis base complex, $F_4S \rightarrow BF_3$ and an ionic salt $[SF_3^+BF_4^-]$ will be considered here.† The principal evidence concerning the constitution of the SF_4–BF_3 adduct can be summarized as follows:

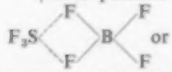
(1) Comparing SF_4 with PF_3 there are two reasons to expect that SF_4 would be much the poorer donor. Firstly, in PF_3 there are only three fluorine atoms tending to decrease the lability of the lone pair whereas in SF_4 there are four. Secondly, there should be less steric hindrance in PF_3 than in SF_4. Nevertheless, while the SF_4 adduct has a dissociation pressure of only ~115 mm at 300°K. BOOTH and WALKUP[5] have shown by thermal analysis that even in the range of −140 to −165°C PF_3 forms no adduct with BF_3.

(2) According to current views of the nature of the co-ordinate link between donor ligands and transition metal atoms or ions, the ability of the ligand to participate in metal-ligand dative π-bonding is often essential to the overall stability of the metal-ligand bonding. Presumably it is always necessary that the ligand have some ability to form a σ-donor bond, but in many cases the π-bond seems to be by far the more important. Thus in PF_3 the phosphorus atom can form $d\pi$-$d\pi$-bonds with metals by using its unfilled $3d_{xy}$ and $3d_{yz}$ orbitals which under the C_{3v} symmetry of PF_3 itself form a doubly degenerate pair of π symmetry. It appears that while the three highly electronegative fluorine atoms greatly reduce the donor power of the phosphorus atom as evidenced by the inability of PF_3 to form complexes with even strong but simple acceptors such as BF_3, they also markedly increase the stability of $d\pi$-$d\pi$ dative bonds. Now in SF_4 the $3d_{xy}$ and $3d_{yz}$ orbitals are again available for π-bonding just as in PF_3 (although they are no longer degenerate). Moreover, the presence of an additional fluorine atom in SF_4 might be expected to further enhance the ability of the sulphur to participate in dative dπ-dπ-bonding. If then it is assumed that the SF_4–BF_3 adduct demonstrated the marked ability of SF_4 to function as a simple σ-donor while the ability of PF_3 to do so is marginal, it is very difficult to understand why PF_3 readily forms stable adducts with $PtCl_2$ whereas BARTLETT and ROBINSON[4a] were unable to effect any combination between $PtCl_2$ and SF_4 or SeF_4.

(3) While BF_3 can function as a fluoride acceptor giving BF_4^- and as a general Lewis acid, and AsF_5 and SbF_5 are known to be very strong F^- acceptors, i.e., acids in the HF system, there is little evidence to show that the latter are also good general Lewis acids. Consequently, it seems reasonable to postulate that the AsF_5

* The term adduct, unmodified by any adjective, is used here with no intended connotation as to the constitution of the substance, since it is the constitution which is at issue.

† It is possible to envision a semi-ionic or ion-pair case in which there are fluoride bridges, viz.



or something similar. Other than the report that the SeF_4–BF_3 adduct is soluble in ether, there is nothing in the literature on SF_4–BF_3 or similar compounds to explicitly suggest the existence of fluorine bridges, nor do we have any such evidence to offer. Consequently, only the two extreme cases are considered. It should be borne in mind however that the essence of arguments favouring the ionic structure or using an ionic structure to explain the course of a reaction would be preserved if some kind of ion-pairing or fluorine bridging exists.

[5] H. S. BOOTH and J. H. WALKUP, *J. Amer. Chem. Soc.* **65**, 2334 (1943).

and SbF_5 adducts of SF_4 are actually $[SF_3^+AsF_6^-]$ and $[SF_3^+SbF_6^-]$ and therefore that these compounds imply the ability of SF_4 to form ionic adducts containing SF_3^+ ions. Moreover, it has recently been shown[6] that the strongest acids in HF, i.e. the best F^- acceptors are AsF_5, SbF_5 *and* BF_3.

(4) Arguments from conductivity data as to the ability of SF_4 to produce SF_3^+ by ionization must be used with caution. The absence of appreciable self-ionization according to

$$2SF_4 = SF_3^+ + SF_5^-$$

could be due entirely to the inability of SF_4 to add a fluoride ion to form SF_5^- and thus not indicate any marked inability to form SF_3^+. For example, the electrical conductivity of BF_3 is very low (5×10^{-10} cm^{-1} ohm^{-1})[7] despite the ready formation of BF_4^- because of its inability to dissociate to give BF_2^+. It is not at all improbable that the inverse situation occurs with SF_4.

(5) Professor F. G. A. Stone of Harvard University has kindly drawn our attention to an additional consideration. If both the SF_4 and SeF_4 adducts with BF_3 are donor-acceptor complexes, the order of stability in this case (Se > S) would be contrary to the general rule that Lewis basicity decreases in descending a group of analogous donors. Of course, if SF_4 and SeF_4 are electron donors, they are unusual in so many other ways that this anomaly would not be very singular. It must be added too that this stability order argument would be irrelevant if the SF_4 adduct is a donor-acceptor complex while the SeF_4 adduct is ionic.

Obviously, direct evidence on the constitution of the SF_4–BF_3 adduct would be desirable. We have attempted to ascertain whether or not BF_4^- ions are present in the solid by infra-red spectroscopy, but the ready dissociation and reactivity toward water have made it impossible to obtain conclusive results. Spectra of both mulls and alkali halide pressings prepared in a nitrogen atmosphere showed bands due to BF_4^- but there is no doubt that decomposition, hydrolytic and otherwise, occurred in the preparation of these mounts. It is rather certain that hydrolysis will lead to the formation of BF_4^-. Attempts to obtain spectra of thin films sublimed onto a silver chloride plate in a vacuum cell also failed to provide useful results. Details will be found in the experimental section.

Physical properties of the SF_4–BF_3 *adduct.* Examination of the infra-red spectrum of the gaseous compound indicated that it is at least 95 per cent dissociated into BF_3 and SF_4 around room temperature and at low pressures. This was confirmed by measurement of the vapour-density at room temperature from which an apparent molecular weight of 85 ± 5 was calculated. The average of the molecular weights of SF_4 and BF_3 is 88. The vapour-pressure as a function of temperature in the range 0–25° was found to follow the equation

$$\log_{10} p_{(mm)} = 12{\cdot}8_4 - \frac{3230}{T}$$

from which the enthalpy of the process

$$(SF_4\text{–}BF_3)_{(s)} = SF_{4(g)} + BF_{3(g)}$$

[6] A. F. Clifford, H. C. Beachell and W. M. Jack, *J. Inorg. Nucl. Chem.* **5**, 57 (1957).
[7] Woolf and Greenwood, *J. Chem. Soc.* 2200 (1950).

is calculated to be 14·8 ± 1 kcal/mole. This is about the order of magnitude to be expected for ($SF_3^+BF_4^-$) by comparison with similar systems. Thus we have

$$[PtCl_4^+, PCl_6^-]_{(s)} = 2PCl_{5(g)} \qquad \Delta H = 21{\cdot}5 \text{ kcal/mole}^{(8)}$$

$$[NO_2^+, NO_3^-]_{(s)} = N_2O_{5(g)} \qquad \Delta H = 13{\cdot}5 \text{ kcal/mole}^{(9)}$$

and from the data of SHEFT *et al.*[10]

$$[BrF_2^+, SbF_6^-]_{(s)} = BrF_{3(g)} + SbF_{5(g)} \qquad \Delta H = 13{\cdot}9 \text{ kcal/mole}$$

In the last case it was not proven that the vapour is fully dissociated but the authors stated that they believed it was and this would certainly seem likely.

Chemical properties of SF_4. Some other chemical properties of SF_4 have been investigated. SF_4 reacts quantitatively with excess F_2 at room temperature and up to at least 250°C to give SF_6. At temperatures up to 300°C no reaction of SF_4 with Cl_2 occurs. SF_4 is apparently not fluorinated by BrF_3 upon bubbling the gas through liquid BrF_3 at room temperature, or after passing the mixed gases through a 15 cm length of monel tubing heated to 300°C, nor does it appear to be more than slightly soluble in BrF_3. This experiment was undertaken to determine whether an adduct such as [$SF_3^+BrF_4^-$] could be readily prepared. It is possible, if SF_4 is sufficiently soluble in BrF_3, that conductivity studies might indicate whether or not SF_3^+ and BrF_4^- ions are present.

SF_4 reacts with BCl_3 at −75°C; at this temperature no evidence of a complex is obtained. Instead SF_4 functions as a fluorinating agent. With SF_4 in excess, the principle reaction is the following:

$$7SF_4 + 4BCl_3 = 4(SF_4{\cdot}BF_3) + 3SCl_2 + 3Cl_2$$

With BCl_3 in excess, mixed halides of boron result. The following equation represents a typical reaction:

$$3SF_4 + 8BCl_3 = 3SCl_2 + 3Cl_2 + 4BF_2Cl + 4BFCl_2$$

The products in these reactions were detected but not quantitatively estimated by their infra-red spectra. It is quite possible that SCl_4 is produced initially but under the experimental conditions it would be expected to decompose rapidly to SCl_2 and Cl_2. With excess BCl_3 a small amount of the (SF_4–BF_3) adduct was also obtained. Since BCl_3 is as least as good a Lewis acid as BF_3 the observed fluorination reaction rather than the formation of any isolable adduct is evidence against SF_4 behaving as a Lewis base. The observed reactions can however be readily explained by assuming that SF_4 functions as an F^- donor, as illustrated in the following reactions:

$$SF_4 + BCl_3 = [SF_3^+BFCl_3^-] = SF_3Cl + BFCl_2$$

$$2BFCl_2 = BF_2Cl + BCl_3$$

$$SF_4 + BFCl_2 = [SF_3^+BF_2Cl_2^-] = SF_3Cl + BF_2Cl$$

$$SF_3Cl + BCl_3 = [SF_2Cl^+BFCl_3^-] = SF_2Cl_2 + BF_2Cl \text{ etc.}$$

It is of course well known that a gaseous system of boron halides containing two

[8] D. P. STEVENSON, *J. Chem. Phys.* **9**, 403 (1941).
[9] *Selected Values of Chemical Thermodynamic Properties.* National Bureau of Standards Circular 500, Washington, D.C. (1952).
[10] I. SHEFT, A. F. MARTIN and J. J. KATZ, *J. Amer. Chem. Soc.* **78**, 1557 (1956).

kinds of halogen rapidly equilibrates to produce all possible mixed halide molecules. It is possible that sulphur(IV) halides also do this. In that case reactions like the last one above need not be postulated. In any event a fluoride ion transfer process like that shown in the first reaction provides a plausible explanation of the over-all fluorination.

EXPERIMENTAL

The apparatus shown in Fig. 1 was used to prepare sulphur tetrafluoride according to the method of BROWN and ROBINSON.[1] Particular attention was given to the

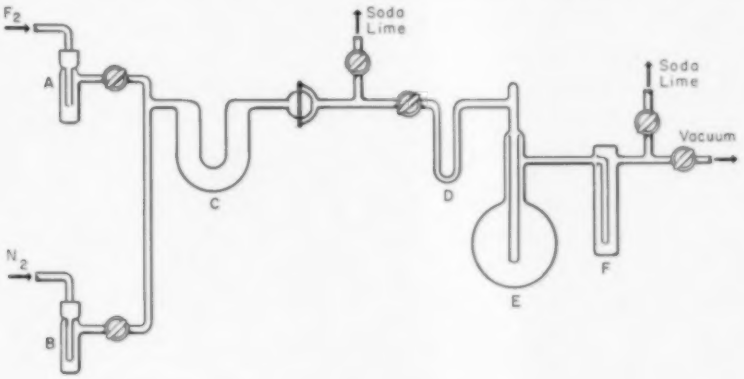


FIG. 1.—Fluorination apparatus

exclusion of moisture and oxygen, the preparation of a thin sulphur sublimate to be treated with fluorine, and the maintenance of low temperature (−75°C) during reaction.

Fluorine from a cylinder (Pennsalt Chemical Co.) was passed through a trap containing NaF pellets to remove HF then bubbled through bubble-counter *A* for flow rate estimation prior to cooling and mixing with dried, deoxygenated nitrogen in U-tube *C*. The gases were further cooled in *D* before reaction with the sulphur sublimate in *E*. The products were trapped in *F*, and non-condensable gases vented through soda-lime traps as indicated. The products were transferred to a vacuum line and a portion of the most volatile part of the sample (SiF_4, SF_6) removed by fractionation. SF_4, together with SOF_2 and other impurities, was present in substantial amount in the middle fraction, with S_2F_{10} concentrating in the lower. For most experiments, samples of the middle fraction were used directly without any attempt at further purification.

Infra-red spectroscopic analysis was employed to analyse gas mixtures throughout this work. Spectra for essentially all likely components of our reaction systems are in the literature. A Baird model AB spectrophotometer was used with an NaCl prism to cover the frequency range 5000 to 700 cm^{-1}, and with a KBr prism between 700 and 400 cm^{-1}.

The SF_4–BF_3 adduct was prepared by condensing impure SF_4 with excess BF_3 (Matheson Co., Inc.) at −195°C. The mixture was warmed to −75°C and impurities in the SF_4 plus excess BF_3 removed by application of vacuum. Attempts were made to prepare Nujol mulls and KBr pellets of the adduct for spectroscopic examination

but, even using drybox techniques, decomposition and/or reaction of the material was always encountered. Presumably this difficulty is related to the moderate vapour pressure of SF_4BF_3 at room temperature, and the extreme sensitivity of SF_4 to traces of moisture. Consequently, the spectra obtained were not necessarily representative of the SF_4BF_3 species. While indication of the BF_4^- ion was obtained from these spectra this must not be taken as structural proof since hydrolysis involving SF_4 and BF_3 would almost certainly give rise to the BF_4^- ion.

Failure to obtain definitive results with the above technique prompted us to try condensing the adduct on a silver chloride disk maintained in a vacuum cell at liquid nitrogen temperature. The spectra obtained using this procedure were either blank or of the gases SF_4, BF_3, SOF_2 and SiF_4. The inability to obtain any new lines in the spectra is ascribed to large particle size of the solid SF_4BF_3 which did condense on the disk, while volatilization of the sample and reaction with moisture and/or Pyrex leads to the presence of the gaseous species.

That SF_4BF_3 is fully dissociated in the gas phase was established by infra-red examination in a gas cell of 10 cm path length, and by measurement of vapour density in a Pyrex bulb of approximately 0·5 l. volume. Only lines ascribed to SF_4 and BF_3 were observed in the spectrum, and the molecular weight values obtained from vapour density data from different trials were 85 and 86. [SF_4, 108; BF_3, 68; average, 88.] The low values may be due to reaction of SF_4 with glass, mercury and moisture producing volatile lower molecular weight species.

The vapour pressure of the compound was measured using an ordinary mercury manometer attached directly to the sample and a vacuum manifold. Suitable baths of ice-water, benzene slush and water at temperatures up to room temperature were used to maintain temperatures in the 0 to 25°C range. Temperatures were determined with a mercury thermometer checked at the ice point. The plot of $\log p$ vs. $1/T$ obeys the relation $\log_{10} p\,(\text{mm Hg}) = 12{\cdot}84 - 3230/T$, and gives an enthalpy of $14{\cdot}8 \pm 1$ kcal/mole.

The reaction of SF_4 with chlorine was studied in two ways. Firstly, known pressures of the two gases (chlorine was purified and dried by passage through $KMnO_4$ solution, conc. H_2SO_4 and P_2O_5) were condensed in a 1 l. Pyrex bulb attached to the vacuum line and to a glass spiral pressure gauge. On warming to room temperature the total pressure was measured. Although such mixtures were heated to 75°C via an infra-red bulb, and also exposed to a strong ultra-violet source for as long as 7 hr, no pressure variations indicative of reaction were observed. Spectroscopic examination of the gases before and after these experiments gave no evidence of new species.

The behaviour of SF_4 and Cl_2 was also studied by passing the gases slowly through a monel metal tube wrapped in heating tape. At temperatures up to 300°C no change in the spectrum of the SF_4 was noted. In contrast, the flow reaction of SF_4 with excess F_2 gave complete conversion to SF_6 even at room temperature.

Using this same apparatus an attempt was made to react BrF_3 with SF_4 by bubbling the latter through the former at room temperature, and subsequently heating the gases passing through the monel tube. Again no significant alteration in the SF_6/SF_4 ratio was shown by infra-red examination, although the slight decrease in the total volume of the SF_4 sample passed through the BrF_3 is suggestive of a small solubility of SF_4 in BrF_3.

The reactions of SF_4 with BCl_3 were studied by condensing the volatile reactants together in a Pyrex tube at −195°C and allowing them to warm to −75°C. At the latter temperature the reaction mixture was liquid except for solid SF_4BF_3 and yellow and the colour grew steadily more intense, due presumably to the formation of SCl_4 and/or SCl_2. Successive fractions of the products were examined spectroscopically in a 10 cm gas cell in the NaCl and KBr regions. The spectra of BCl_3, BF_3 and the mixed halides have been reported in detail by LINDEMAN and WILSON,[11] and the Raman spectrum of SCl_2 by STAMMREICH *et al.*[12]

[11] L. LINDEMAN and M. K. WILSON, *J. Chem. Phys.* **24**, 242 (1956).
[12] H. STAMMREICH, R. FORNERIS and K. SONE, *J. Chem. Phys.* **23**, 972 (1955).

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REACTIONS OF CARBON DIOXIDE WITH SODIUM AND LITHIUM BOROHYDRIDES*

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Abstract—Sodium borohydride reacts with excess carbon dioxide in the absence of solvent at temperatures somewhat above room temperature to form a fluffy white solid which is thought to be sodium formatomethoxyborate, ($NaBO(OCH^3)(O^2CH)$). When the temperature is lowered, and dimethyl ether is used as a solvent, the reaction product is sodium triformatoborohydride, $NaHB(O_2CH)_3$. Various other reactions of carbon oxides and sulphides with double hydrides are discussed.

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ALTHOUGH a number of carbon dioxide reductions with so called double hydrides, especially lithium aluminium hydride[1,2,3] and lithium borohydride,[4] have been reported, few, if any, attempts have been made to isolate or identify intermediates, i.e., the materials whose hydrolyses yield the free organic end products. This is probably due to the difficulty in working with solids of this type and to their rather low thermal stabilities. In the course of investigations of certain double hydride–carbon dioxide reactions, the authors have isolated several of these intermediates in the hope that the results obtained might prove useful in interpreting reduction reactions and modes of decomposition of intermediates.

Strangely enough, in the investigations to be described, the behaviour of a given double hydride with carbon dioxide provided little basis for prediction of the behaviour of another double hydride with the same substance, since almost every reaction seemed to be unique. Further, a given double hydride could be made to yield entirely different products with carbon dioxide, depending upon the conditions employed.

Sodium borohydride and carbon dioxide in the absence of solvents

When sodium borohydride and excess carbon dioxide are allowed to stand together in a glass tube at temperatures somewhat above room temperature, a reaction, characterized by an increase in the apparent volume of the solid, occurs. A preliminary description of this reaction has previously been presented by WARTIK and PEARSON.[5] Two moles of carbon dioxide are absorbed for every mole of sodium borohydride used (Table 1).

Although the nature of the reaction product, a fluffy white solid, has not been

* Taken in part from a Ph.D thesis submitted by R. K. PEARSON to the Graduate School of the Pennsylvania State University, August 1955.

(1) R. N. NYSTROM, W. H. YANKO and W. G. BROWN, *J. Amer. Chem. Soc.* **70**, 441 (1948).
(2) J. D. COX and R. J. WARNE, *J. Chem. Soc.* 3167 (1950).
(3) A. E. FINHOLT and E. C. JACOBSON, *J. Amer. Chem. Soc.* **74**, 2943 (1952).
(4) J. G. BURR, W. G. BROWN and H. E. HELLER, *J. Amer. Chem. Soc.* **72**, 2560 (1950).
(5) T. WARTIK and R. K. PEARSON, *J. Amer. Chem. Soc.* **77**, 1075 (1955).

directly established, there is good reason to suggest that it is ($NaBO(OCH_3)(O_2CH)$)* and to regard it as a substituted borohydride of a type not previously reported. This product is somewhat unstable at temperatures necessary to bring the reaction to rapid completion, the volatile substances resulting from its decomposition being methyl formate and methyl borate.

TABLE 1.—THE REACTION OF SODIUM BOROHYDRIDE AND EXCESS CARBON DIOXIDE IN THE ABSENCE OF A SOLVENT

Exp.	Time (hr)	Temp. (°C)	$NaBH_4$ used mmoles	CO_2 used mmoles	CO_2 rec. mmoles	Reaction ratio CO_2/$NaBH_4$	$B(OCH_3)_3$ obtained per mmole CO_2 consumed mmoles	HCO_2CH_3 obtained per mmole CO_2 consumed mmoles
1	11·25	125	2·935	8·75	2·905	1·995	0·0673	0·0373
2	11·25	125	2·860	8·55	2·867	1·992	0·0665	0·0296
3	14	117	9·37	19·59	1·325	1·95	0·0677	0·0253
4	24	120–125	13·39	30·03	3·92	1·95	0·0676	0·0293
5	18	123	14·01	31·76	5·30	1·89	0·0569	0·0348
6	22·5	123	11·35	31·50	9·22	1·935	0·0516	0·0384
7	16	125	9·65	25·2	6·31	1·96	0·0655	0·0292
8	120	70±10	13·42	29·87	4·55	1·89	0·01745	0·0214

Evidence supporting the assigned empirical formula for the reaction product may by summarized as follows:

1. The observed stoicheiometry of the reactants is in accord with the equation for the formation of a material with the assumed formula:

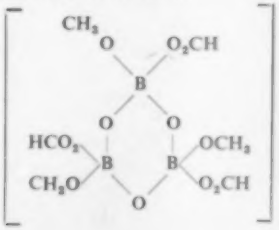
$$NaBH_4 + 2CO_2 \rightarrow NaBO(OCH_3)(O_2CH).$$

2. Hydrolysis of the reaction product yields the appropriate amount of methyl alcohol, according to the equation:

$$NaBO(OCH_3)(O_2CH) + 2H_2O \rightarrow NaO_2CH + H_3BO_3 + CH_3OH.$$

Thus in the hydrolysis, after correction had been made for the small amount of decomposed product, it was found that 52·3 per cent (average of two experiments) of the carbon originally used as carbon dioxide had been converted to methoxy groups. This is in satisfactory agreement with the given equation.

* Although the product has tentatively been assigned to the formula shown, it is possible that it is a one-to-one mixture of $NaBO_2$ and the hitherto unreported $NaB(OCH_3)_2(O_2CH)_2$. Still another possibility is $Na_2B_2O_2(OCH_3)_2(O_2CH)_2$, for which the anion structure



seems reasonable.

3. The quantity of formic acid released during acid hydrolysis of the reaction product can be accounted for in terms of the assigned formula (48·6 per cent of the carbon dioxide was converted to formate).

As mentioned above, the solid product undergoes slight decomposition at temperatures high enough to permit rapid completion of the reaction. For this reason, the values given above include corrections made for the presence of solid decomposition products. (The basis for these corrections is described in the experimental section.)

The thermal decomposition of the solid product yields two volatile substances, methyl borate and methyl formate. These, apparently, are the result of two separate decomposition paths, equations for which follow:

$$3NaBO(OCH_3)(O_2CH) \rightarrow 3NaO_2CH + B_2O_3 + B(OCH_3)_3$$

$$NaBO(OCH_3)(O_2CH) \rightarrow NaBO_2 + HCO_2CH_3.$$

The first decomposition reaction seems to be quite temperature dependent, since the amount of methyl borate formed during the initial reaction may be greatly decreased by lowering the reaction temperature.

Attempts to recrystallize the reaction product from various solvents were not successful, since the solid, in most cases, was not significantly soluble in the solvents used (diethyl ether, benzene, *iso*propylamine and dimethoxyethane). Methyl alcohol, though it did dissolve the solid product completely, did so by reacting with it, since most of the boron in the original solid was converted to volatile methyl borate. The solid dissolved partially in ammonia, but it was not established whether this was due to reaction with the solvent or to selective dissolution of components of a mixture.

Finally, it may be mentioned that, when the original reaction was carried out using an excess of sodium borohydride, rather than carbon dioxide, more than half of the carbon used (up to 59 per cent) was converted to methoxy groups.

Reaction of sodium borohydride with carbon dioxide in dimethyl ether

The course of the reaction between sodium borohydride and excess carbon dioxide is different when the temperature is lowered to 25°C or below, and dimethyl ether is used as a solvent. Under these conditions, three, instead of two, moles of carbon dioxide are absorbed per mole of sodium borohydride, and the product is a powdery white solid with a volume about six to eight times as great as the sodium borohydride originally used. Acid hydrolysis of the solid results in formation of hydrogen, boric acid, and formic acid in quantities consistent with the formula $NaBH(O_2CH)_3$.

It is believed that this product represents the first reported isolation of a formatoborohydride. Although this material seems reasonably stable, it was observed that prolonging the reaction time lowered the purity of the sodium triformatoborohydride.

Methyl formate was the principal volatile product of the thermal decomposition of the solid, but another less volatile material was also formed. Although the latter material was not thoroughly investigated, on standing at room temperature it appeared to decompose to evolve methyl formate. The following mode of decomposition is suggested to explain these observations:

$$NaBH(O_2CH)_3 \rightarrow NaO_2CH + HB(O_2CH)_2$$

$$2HB(O_2CH)_2 \rightarrow HCO_2CH_3 + \text{other products.}$$

Further reactions involving sodium borohydride

Carbon monoxide, carbonyl sulphide and carbon disulphide do not appear to react with sodium borohydride in the absence of a solvent at 125°C for periods of time comparable to those used with carbon dioxide.

Carbon disulphide, however, does react with sodium borohydride when dimethyl ether is present as a solvent. A detailed description will appear in a subsequent publication.

Reaction involving lithium borohydride

Lithium borohydride was observed to take up carbon dioxide slowly in the absence of a solvent at 120°C. The observed molar reaction ratio of carbon dioxide to lithium borohydride was 1·56 to 1·00, and the quantity of formate obtained from the solid reaction product represented 22·5 per cent of the carbon from the carbon dioxide converted. A small quantity of diborane, and probably dimethoxyborane, were produced in side reactions. However, it is likely that the principal reaction was

$$5LiBH_4 + 8CO_2 \rightarrow 2LiB(OCH_3)_3(O_2CH) + 3LiBO_2.$$

When ethyl ether was used as a solvent in a sealed-tube reaction between lithium borohydride and excess carbon dioxide, a reaction ratio of 2·12 moles of carbon dioxide to 1·00 mole of lithium borohydride was observed. Again, small quantities of diborane, methyl borate, and probably dimethoxyborane, resulted. The ratio of formate produced to lithium borohydride consumed was 1·05 to 1·00. This suggests that the principal reaction is similar to that of sodium borohydride and carbon dioxide at 125°C.

$$LiBH_4 + 2CO_2 \rightarrow LiBO(OCH_3)(O_2CH)$$

EXPERIMENTAL

Preparation and purification of reagents

Sodium borohydride was obtained from Callery Chemical Company and was purified by extraction of the crude solid with *iso*propyl amine. After filtration of the solution, the amine was distilled off and the last traces were removed by pumping at 100°C for 1 hr. Samples of the borohydride purified in this manner, when treated with 6 M hydrochloric acid, in every case liberated more than 95 per cent of the theoretical volume of hydrogen.

Carbon dioxide was obtained from commercial dry ice by sublimation from a flask kept at −78·5°C and passage of the vapours through a U-trap cooled to −78·5°C. After passing the material obtained in this way through a U-trap held at −111·9°C, its vapour pressure at −111·9°C was 27·4 mm (reported value[6] 27·4 mm).

Dimethyl ether, obtained from the Matheson Company, was passed through a U-trap held at −78·5°C. Part of the material which passed through this trap was distilled away until the residue had a vapour-pressure of 281·0 mm at −45°C (reported value 277 mm[7]).

Lithium borohydride was prepared metathetically from sodium borohydride and lithium chloride by the method of SCHLESINGER *et al.*[8] Samples subjected to hydrolysis liberated 93·6 per cent of the theoretical volume of hydrogen.

[6] *International Critical Tables*, Vol. 3, p. 207. McGraw-Hill, New York (1928).
[7] *International Critical Tables*, Vol. 3, p. 216. McGraw-Hill, New York (1928).
[8] H. I. SCHLESINGER, H. C. BROWN and E. K. HYDE, *J. Amer. Chem. Soc.* **75**, 209 (1953).

Reaction of sodium borohydride with excess carbon dioxide in the absence of solvent

In a typical experiment, a weighed quantity of sodium borohydride (2·86 mmoles) was introduced into a 250 ml nitrogen-filled reaction flask. After removal of the nitrogen on the vacuum system, the reaction flask was maintained at 105°C for 3 hr with pumping to drive off traces of water absorbed by the sodium borohydride. Carbon dioxide (8·55 mmoles) was now condensed in the reaction vessel by cooling and the latter was sealed. The flask was then placed in an oven at 125°C for 11·25 hr. During this time the volume of its solid contents swelled to approximately three times that of the sodium borohydride used.

The flask was then cooled to liquid nitrogen temperature, opened to the vacuum system, and the trace of non-condensible gas present was removed by pumping. The volatile contents of the flask were separated by passage through U-traps held at −22·9°, −78·5°, −111·9° and −196°C. The material in the −196°C U-trap proved to be unchanged carbon dioxide (2·87 mmoles, vapour-pressure = 28·3 mm at −111·9°C, reported value 27·4 mm[9]). The material in the −111·9°C U-trap (0·168 mmoles) was shown to be methyl formate (vapour-pressure at −22·9°C = 53·5 mm, reported value 56 mm,[10] molecular weight by vapour-density 62·3, calculated 60·0). The material in the −78·5°C U-trap (0·378 mmoles) was methyl borate (vapour-pressure 34·5 mm at 0°C, reported value 37·9 mm[11]). The observed molecular weight (by vapour density) of methyl borate obtained from a subsequent identical experiment was 101 (calc. 103·8). The molar reaction ratio of carbon dioxide to sodium borohydride was 1·99 to 1·00.

The non-volatile white solid reaction product was hydrolysed by condensing an excess of water in the reaction flask, resealing the latter, and heating for 3 hr on the steam bath. The extremely small volume of hydrogen (only 0·5 per cent of the hydrogen available from the sodium borohydride used) obtained when the flask was opened indicated that essentially all the hydridic hydrogen had been consumed by reaction with carbon dioxide.

The volatile products of the hydrolysis were then separated by repeated passage of the water–methanol mixture through a U-trap at −45°C. Methanol (1·652 mmoles) was identified by its vapour-pressure of 28·9 mm at 0°C (reported value for methanol 29·6 mm) and by its molecular weight 32·7 (calc. for CH_3OH ≒ 32·04). It was found that essentially half* (52 per cent) of the carbon from the carbon dioxide which had reacted had been converted to methoxy groups.

A number of experiments were carried out in a manner similar to that described above, and the results are shown in Table 1. Changing the reaction time from 11·25 to 24 hr had little effect on reaction ratio of carbon dioxide to sodium borohydride or on the quantities of methyl borate and methyl formate. Reproducibility of the quantity of carbon dioxide used and of the methyl borate and methyl formate formed was excellent.

* This value was obtained by adding the number of mmoles of methoxy group obtained as methanol to the number of mmoles of methoxy groups from the volatile reaction products (methyl borate and methyl formate).

[9] *International Critical Tables*, Vol. 3, p. 207. McGraw-Hill, New York (1928).
[10] *International Critical Tables*, Vol. 3, p. 207. McGraw-Hill, New York (1928).
[11] S. H. WEBSTER and L. M. DENNIS, *J. Amer. Chem. Soc.* **55**, 3233 (1933).

As shown by Exp. 8, the reaction rate was much lower at 70° ± 10°C. Under these conditions, a slightly lower CO_2 to $NaBH_4$ ratio (1·89) was obtained, indicating that even after 120 hr reaction was not quite complete. Although the relative quantity of methyl formate was not greatly affected by lowering the temperature, a substantially smaller amount of methyl borate was obtained. These observations suggest that the compound formed from the reaction of carbon dioxide and sodium borohydride was undergoing thermal decomposition at the temperatures needed to obtain conveniently rapid reaction. A typical analysis for formate group was carried out as follows: The solid non-volatile product (1·308 g) of Exp. 7 (Table 1) was hydrolysed with excess water. Only a trace of hydrogen resulted from this hydrolysis. The remaining volatile products were removed by evacuation of the hydrolysis vessel for 7 hr at 25°C. The solid product of the hydrolysis was then washed out of the vessel and diluted to 100 ml in a volumetric flask.

The determination of the formate group was made in three ways, the first of which involved oxidation with a standard solution of permanganate.[12]

With a 25 ml aliquot of the above solution, it was found that 9·04 mmoles of formate was present in the entire hydrolysis product. It was determined that 50·3 per cent of the carbon* of carbon dioxide used in reaction with sodium borohydride had been converted to formate.

Confirmation of the above result was obtained in the following manner: Another 25 ml portion of the solution of hydrolysis product was treated with 5 ml of concentrated sulphuric acid and the solution was evaporated on the vacuum system to the point where it exhibited negligible vapour-pressure. The water and formic acid evolved were caught in U-traps at −196°C. An additional 15 ml of water was added to the residue and evaporated, again retaining the distillate at −196°C. Titration of the distillate with standard base showed that 8·64 mmoles of formic acid was present in the hydrolysis product. Addition of the small quantity of formate group which appeared as methyl formate in the original reaction showed that 48·1 per cent of the carbon of the carbon dioxide used in the reaction with sodium borohydride had been converted to formate. In still another experiment, after the solid reaction product had been treated with methanol, the resulting non-volatile solid product was allowed to react with concentrated sulphuric acid. Carbon monoxide was evolved in such quantity that, by the above method of calculation, 47·5 per cent of the carbon of the carbon dioxide used was found to have been converted to formate. Thus, the average of the three different methods for determination of carbon dioxide converted to formate was 48·6 per cent.

Solubility studies

In an effort to determine whether the sodium borohydride–carbon dioxide reaction product was a substance or a mixture, its solubility in various solvents was studied with the expectation that, if it proved to be a mixture, one of its components might be removed by extraction. Portions of the solid were subjected to extraction procedures with ethyl ether, *iso*propyl amine, dimethoxyethane, benzene, methanol and liquid ammonia. The first four did not dissolve the solid significantly. Methanol, although it

* This value was obtained by adding the number of mmoles of formate from the solid hydrolysis product to the number of mmoles of formate of the methyl formate previously isolated.

[12] H. C. Jones, *J. Amer. Chem. Soc.* **17**, 539 (1895).

completely dissolved the solid, did so by reaction with it (84 per cent of its boron appeared in the form of methyl borate). The solid dissolved partially in liquid ammonia, and after exhaustive extraction, the insoluble portions in two different experiments were found to contain 18·4 per cent and 20·36 per cent boron (calc. for $NaBO_2$ ≒ 15·85%). These experiments did not establish whether the solubility in ammonia was due to reaction with the solvent (as in the case of methanol) or to selective dissolution of components of a mixture.

Thermal decomposition of $NaBO(OCH_3)(O_2CH)$

A 269·3 mg sample of sodium formatomethoxyborate (product of Exp. 4, Table 1) was heated for 26 hr in a sealed container at 300°C. This treatment yielded 0·356 mmoles of methyl borate and 0·264 mmoles of methylformate. The total quantities of methyl borate and methyl formate released during the reaction of carbon dioxide and sodium borohydride and during the pyrolyses of the solid product are as follows:

	Released during original preparation	Released in pyrolyses at 300°C	Total
$B(OCH_3)_3$	0·318 mmole	0·356 mmole	0·674 mmole
HCO_2CH_3	0·138 mmole	0·264 mmole	0·402 mmole

Since the weight of sample in this pyrolysis corresponded to 2·42 mmoles of $NaBO(OCH_3)(O_2CH)$, it can be seen that exactly the same molar quantity of methoxide ($3 \times 0{\cdot}674 + 0{\cdot}402 = 2{\cdot}42$ mmoles) was released during its thermal decomposition. The quantity of formate released (0·402 mmoles) bore no simple relationship to the quantity of sodium formatomethoxyborate.

Reaction of sodium borohydride with carbon dioxide in dimethyl ether

Sodium borohydride (14·94 mmoles) was placed in a 200 ml nitrogen-filled reaction vessel made of thick-walled Pyrex tubing, along with a magnetic stirring bar. The loading tube was sealed, the vessel was evacuated, and 85·8 mmoles of carbon dioxide along with 9·467 g of dimethyl ether, was condensed into the reaction vessel by cooling to −196°C. After the constriction had been sealed, the vessel was allowed to warm slowly to room temperature, and, as soon as the mixture was melted, the magnetic stirrer was set in motion. Stirring at room temperature was continued for a period of 36 hr, during which time the solid in the vessel swelled to about six to eight times the volume of the original sodium borohydride.

The reaction vessel was opened to the vacuum system and a small volume (approximately 0·3 mmoles) of non-condensable gas was removed by pumping. The remaining volatile material was separated by fractional condensation using bath temperatures of −135° and −196°C. Carbon dioxide (41·0 mmoles) was obtained in the −196°C U-trap (vapour-pressure at −111·9°C ≒ 28·4 mm). Thus, the molar reaction ratio of carbon dioxide to sodium borohydride was 2·99 to 1·00.

Treatment of the white solid remaining in the flask with hydrochloric acid produced 5·54 mmoles of hydrogen; when the solid was treated with dilute sulphuric acid,

5·94 mmoles of boric acid and 16·49 mmoles of formic acid were obtained (all values based on 1 g of sample).

	Observed (mmoles/g)	Calculated for $NaHB(O_2CH)_3$(mmoles/g)
Formic acid	16·49	17·69
H_2 from Hydrolysis	5·54	5·89
Boric acid	5·94	5·89

A second reaction, carried out in a similar fashion, yielded almost identical results.

Thermal decomposition of $NaBH(O_2CH)_3$

A portion (0·3902 g) of the solid product of the reaction of sodium borohydride and excess carbon dioxide in dimethyl ether from the former experiment was heated with pumping. A condensable gas was evolved at temperatures above 80°C. After 9 hr of heating at 150°C and pumping through cold traps at −196°C, the volatile-condensable products of decomposition were passed through U-traps at −78·5°, −111·9°C and −196°C. The product retained in the U-trap at −111·9°C was shown to be methyl formate by its vapour-pressure of 54 mm (reported value 56 mm) at −22·9°C and its molecular weight of 62·8 (calc. 60·0). The material trapped in the −78·5°C U-trap showed a vapour-pressure of about 10 mm at 0°C; however, this vapour-pressure value changed quickly on standing, and subsequent experiments showed that this material decomposes to methyl formate. A small quantity (0·146 mmoles) of gaseous material remained in the U-trap at −196°C and was observed to melt to a liquid when warmed. This property suggested that it was not carbon dioxide, although its vapour-pressure at −111·9°C was 27·6 mm. The liquid of lesser volatility which evolves methyl formate on standing may be diformatoborane.

Lithium borohydride reactions

Since the procedures employed here were similar to those used for sodium borohydride reactions, and since the results obtained are given in the foregoing discussion, no further description of experimental work will be presented.

J. Inorg. Nucl. Chem., 1958, Vol. 7, pp. 412 to 417. Pergamon Press Ltd., London

BEITRÄGE ZU DEN EIGENSCHAFTEN DES VIERWERTIGEN CHROMS

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Abstract—During their investigations into chromium ^{IV} the authors found that the rate of disproportionation is influenced by the dissociation of Cr^{IV} trimers. Because of this dissociation the absorption spectrum of Cr^{IV} cannot be accurately determined. The calculating procedure allows to determine only qualitatively the absorption spectrum of Cr^{IV}.

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IN unserer ersten Arbeit berichteten wir über reaktionskinetische Untersuchungen einiger Chromatoxydationen in stark schwefelsauren Lösungen.[1] Wir stellten auf Grund der spektrophotometrisch bestimmten Reaktionsgeschwindigkeit fest, dass das Chromat unter Bildung vierwertigen Chroms an den Oxydationsreaktionen teilnimmt. In diesem Zusammenhange brachten wir ein prinzipielles Verfahren in Vorschlag mit dessen Hilfe das Absorptionsspektrum der intermediär auftretenden vierwertigen Chromverbindung bestimmt werden könnte. Unsere Ergebnisse bezogen sich nur auf den Fall, wenn die Reduktion des Chromats in stark saurer Lösung verläuft, d.h. wo *iso*polychromsäuregruppen auftreten. Die Chromsäure nimmt in neutraler oder alkalischer Lösung einem anderen Mechanismus entsprechend teil. Nach BAILEY und SYMONS[2] verläuft die Reduktion des Chromats in stark alkalischer Lösung über das fünfwertige Chrom. Das sich im Verlaufe der Reaktion gebildete fünfwertige Chrom unterliegt in wässriger Lösung einer raschen Disproportionierung zu sechs- und dreiwertigem.

Im folgenden haben wir uns zum Ziele gesetzt die Eigenschaften des Cr^{IV}, besonders aber dessen Absorptionsspektrum näher zu untersuchen, bzw. zu bestimmen und dementsprechend die Kinetik der Cr^{IV} Disproportionierung einer eingehenden Analyse zu unterziehen. Die Disproportionierung kann, wie das schon in unserer ersten Arbeit und seither öfters festgestellt wurde—Konzentrationsbereich 10^{-3} Mol/l. Cr^{VI}—mit einer reaktionskinetischen Gleichung ersten Grades ausgedrückt werden. Aus den Angaben der ersten Arbeit geht hervor, dass die Bestimmung der Geschwindigkeitskonstanten nur mit einer Genauigkeit von $\pm$10–15% erfolgte. Die Streuung der Ergebnisse kann im Falle kleiner Reaktionsgeschwindigkeiten der Ungenauigkeit der Extinktionsmessung zugeschrieben werden. Eine eingehende Fehleranalyse zeigte, dass der Extinktionsmessungsfehler eine Streuung der Geschwindigkeitskonstante höchstens von 1–1,5% nach sich ziehen kann. Interessant ist die graphische Darstellung der Geschwindigkeitskonstante als Funktion der Reaktionsdauer bzw. der mit ihr

[1] E. PUNGOR und J. TROMPLER, *J. Inorg. Nucl. Chem.* **5**, 123 (1957).
[2] N. BAILEY und M. C. R. SYMONS, *J. Chem. Soc.* 203 (1957).

im Zusammenhang stehenden Cr^{IV}-Konzentration. (Siehe Abb. 1.) Zu den arithmetischen Mittelwerten der bei der Rechnung herangezogenen Zeitpunkten wurden die entsprechenden, einer kinetischen Untersuchung zu Grunde liegenden und berechneten Geschwindigkeitskonstanten aufgetragen. Aus Abb. 1 ist zu ersehen, dass die Geschwindigkeitskonstanten mit sinkender Cr^{IV}-Konzentration kleiner werden. Diese Tatsache forderte eine erneute und umfassendere Untersuchung der kinetischen Gleichung.

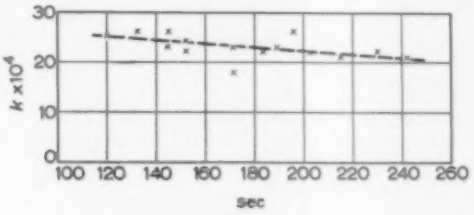

Abb. 1.

Die Messungen wurden am Spektrophotometer Beckman DU ausgeführt und zwar bei Extinktionswerten von etwa 1. Lösungen höherer Chrom^{IV}-Konzentration konnten daher nur nach entsprechender Verdünnung in die uns zur Verfügung stehenden 1cm Küvetten gefüllt und der Messung zugeführt werden.

BESCHREIBUNG DES VERFAHRENS

Alle Untersuchungen wurden, den Erfahrungen unserer ersten Versuche gemäss, in 78%-iger schwefelsaurer Lösung durchgeführt. Das Verfahren unterschied sich von dem bereits in der ersten Arbeit beschriebenen nur insofern, als dass die höher konzentrierten Lösungen entsprechend verdünnt werden mussten. Die Versuche wurden mit gereinigtem Kaliumbichromat und mit Natriumformiat p.a. nach Merck, beide in 78%-iger gereinigter Schwefelsäure[3] gelöst, durchgeführt. Es wurde nur ein Teil der zum Versuch angewandten Chromsäure reduziert, d.h. die Reaktionspartner so vermengt, dass immer Chromat im Überschuss blieb. Als grösste Chromatkonzentration wurde $2{,}4 \cdot 10^{-2}$ Mol/l. gewählt. Es erwies sich als zweckmässig die spektrophotometrischen Messungen bei einer Chromatkonzentrationen von $2{,}4 \cdot 10^{-3}$ Mol/l. durchzuführen. Im Falle konzentrierterer Lösungen wurde die Reaktionsmischung nach Zufügen schwefelsaurer Ameisensäurelösung—2 Minuten Wartezeit—mit 78%-iger H_2SO_4 auf $2{,}4 \cdot 10^{-3}$ Mol/l. Ausgangskonzentration verdünnt. Die Geschwindigkeitskonstante der Disproportionierungsreaktion konnte auf Grund photometrischer Messungen berechnet und die Lichtabsorption der Lösung auf den Verdünnungszeitpunkt extrapoliert werden. Der Fehler, den die Unsicherheit des Verdünnungszeitpunktes von 3 Sekunden verursachte, konnte neben der Reaktionsdauer von 120 Sekunden vernachlässigt werden. Es konnte unter Anwendung der sich auf den Verdünnungszeitpunkt beziehenden Extinktion die Chrom^{IV}-Konzentration berechnet werden. Ausserdem konnte, unter Berücksichtigung der angewandten Chromat—und Formiatmenge die Anfangskonzentration des Cr^{IV} bestimmt werden. Das Rechenverfahren lieferte unter zuhilfenahme des Verdünnungszeitpunktes die Geschwindigkeitskonstante der Disproportionierung in den konzentrierteren Reaktionslösungen.

[3] E. Schulek und F. Szeghö, *Z. Anal. Chem.* **123**, 252 (1942).

AUSWERTUNG DER ERGEBNISSE

Die zweite Kolonne der Tabelle 1 enthält die Geschwindigkeitskonstanten der Disproportionierungsreaktion im Falle verschiedener Cr^{IV}-Konzentrationen. Es ist daraus zu ersehen, dass sich die nach einer Geschwindigkeitsgleichung ersten Grades berechnete Konstante mit der Cr^{IV}-Konzentration ändert. Berechnungen mit reaktionskinetischen Gleichungen höheren Grades verliefen erneut ergebnislos, d.h. aus

TABELLE 1

Konzentration des Cr^{IV} zu Beginn der Dispr. (Mol/l.)	Berechnete Geschwindigkeitskonstante (nach erster Ordnung) k (sec^{-1})	Dissoziationsgrad der Cr^{IV}-Trimere α	k_α	k_α Mittelwert
$7{,}7 \cdot 10^{-4}$	$1{,}2 \cdot 10^{-3}$	0,933	$1{,}79 \cdot 10^{-2}$	
$9{,}4 \cdot 10^{-4}$	$1{,}9 \cdot 10^{-3}$	0,920	$2{,}39 \cdot 10^{-2}$	
$1{,}4 \cdot 10^{-3}$	$2{,}3 \cdot 10^{-3}$	0,889	$2{,}08 \cdot 10^{-2}$	$2{,}04 \cdot 10^{-2}$
$2{,}1 \cdot 10^{-3}$	$3{,}1 \cdot 10^{-3}$	0,849	$2{,}05 \cdot 10^{-2}$	
$4{,}2 \cdot 10^{-3}$	$4{,}3 \cdot 10^{-3}$	0,758	$1{,}78 \cdot 10^{-2}$	
$2{,}1 \cdot 10^{-2}$	$1{,}1 \cdot 10^{-2}$	0,492	$2{,}16 \cdot 10^{-2}$	

den Werten der Geschwindigkeitskonstanten konnte auf keine ganzzahlige Reaktionsordnung geschlossen werden. Im Falle kleiner Konzentrationsänderungen erwies sich die Konstantenberechnung nach einer Gleichung ersten Grades als einzige Lösung.

Im Verlaufe der weiteren Berechnungen nahmen wir an, dass das Dissoziationsgleichgewicht der Hypochromat^{IV}-Polymere eine Änderung der Geschwindigkeitskonstante verursacht.

Diesem Gedanken folgend nahmen wir an, dass das Cr^{IV} nur dann einer Reaktion ersten Grades entsprechend disproportionieren kann, wenn sich im noch unzersetzten Molekül drei Cr^{IV} aneinander binden. Wenn daher Cr^{IV}-Trimere auftreten—Handbücher weisen im Falle des Cr^{VI} bereits darauf hin[4]—so kann als erster Schritt folgendes Dissoziationsgleichgewicht, das natürlich eine Funktion der Cr^{IV}-Konzentration ist, angenommen werden.

$$Cr_3^{IV} \rightleftharpoons Cr_2^{IV} + Cr^{IV}$$

Es ist bekannt, dass das Cr_2^{VI}, im Falle des sechswertigen Chroms schon in schwach sauren Lösungen stabil ist. Obwohl unsere Kenntnisse auf dem Gebiete der Cr^{IV} *Iso*polysäure klein sind, darf angenommen werden, dass das dimere Cr^{IV} unter den herrschenden Bedingungen—78% H_2SO_4—nur in sehr geringem Masse dissoziiert.

Vom Standpunkte der Disproportionierung kommen also nur die Trimere in Betracht. Ihre Dissoziation muss in der Disproportionierungsgleichung berücksichtigt werden. Die Geschwindigkeit der Dissoziationsgleichgewichtseinstellung darf

[4] E. H. RIESENFELD, *Lehrbuch der anorganischen Chemie* p. 522. Rascher Verlag, Zürich (1946); W. HÜCKEL, *Anorganische Structurchemie* p. 158. F. Enke Verlag, Stuttgart (1948).

im Verhältnis zur Geschwindigkeit der Disproportionierung als sehr gross angenommen werden.

$$-\frac{dC_{IV}}{dt} = k_0/1 - \alpha/C_{IV,t}$$

wo α nach folgender Dissoziationsgleichung bestimmt wird.

$$K = \frac{\alpha^2}{1-\alpha} C_{IV}$$

Für K wurde auf Grund unserer Berechnungen der Wert von $1 \cdot 10^{-2}$ gefunden. In Kolonne 3 und 4 der Tabelle 1. stellten wir die diesbezüglichen Rechenergebnisse zusammen, d.h. die den verschiedenen Cr^{IV}-Konzentrationen entsprechenden α und k_0 Werte. k_0 wurde nach folgender Gleichung berechnet:

$$k_0 = \frac{k}{1-\alpha}$$

wo α den Dissoziationsgrad, k hingegen die aktuelle Geschwindigkeitskonstante bedeutet. Die Werte für k_0 schliessen natürlich alle schon vorher erwähnten Bestimmungsfehler von k in sich ein.* Der Mittelfehler der einzelnen k_0-Werte beträgt etwa 10%, der des Mittelwertes hingegen liegt unterhalb 5%. Dieses Ergebnis darf als zufriedenstellend betrachtet werden, d.h. die Annahme der Theorie des Cr^{IV}-Dissoziationsgleichgewichtes als Grundlage der mathematischen Ableitung und reaktionskinetischen Interpretierung kann mit Recht als bewiesen gelten.

Wir suchten für das Auftreten des Dissoziationsgleichgewichtes ausser den oben angeführten noch andere, näher liegende Beweise zu erlangen. Es zeigte sich während der Verdünnungsversuche, dass die erhaltenen Lösungen in viel geringerem Masse farbig sind, als dies auf Grund der Verdünnung zu erwarten war. Eingehendere spektrophotometrische Messungen bewiesen dies endeutig. Die Messungen wurden in 78%-iger schwefelsaurer Lösung folgendermassen durchgeführt: $2{,}7 \cdot 10^{-2}$ Mol/l. Chromat und $2{,}5 \cdot 10^{-2}$ Mol/l. Formiat wurden zur Reaktion gebracht. Nach 180 Sekunden—mit 3 Sekunden Genauigkeit—verdünnten wir die so erhaltenen Reaktionslösungen auf das fünf- und zehnfache. Die Verdünnung wurde selbstverständlich mit 78%-iger Schwefelsäure durchgeführt. An beiden Lösungen verfolgten wir die Disproportionierung spektrophotometrisch bei der Wellenlänge von 440 mμ. Die Messergebnisse, auf den Verdünnungszeitpunkt extrapoliert, ergaben, dass die Extinktion der fünffach verdünnten Lösung $1{,}71 \pm 0{,}03$, die der zehnfach verdünnten hingegen $0{,}730 \pm 0{,}002$ betrug. Nach drei Stunden, bzw. nach Reaktionsende massen wir $E\infty$. Für diese ergab sich 1,07 und 0,532. Das Verhältnis dieser $E\infty$ Messergebnisse entspricht dem des Verdünnungsverhältnisses, was natürlich bedeutet, dass sich der molare Extinktionskoeffizient des Cr^{IV} und Cr^{III} mit der Verdünnung nicht ändert. Zum Zeitpunkte der fünf und zehnfachen Verdünnung betrug die errechnete Cr^{IV}-Konzentration im ersten Falle $1{,}3 \cdot 10^{-3}$ Mol/l. und im zweiten $0{,}65 \cdot 10^{-3}$ Mol/l. Daraus ergibt sich für den Extinktionskoeffizienten der Wert von 700 und 500. Die Änderung des Dissoziationsgrades zieht also eine Verschiebung des molaren Extinktionskoeffizienten nach sich.

* Der Fehler, der bei der Berechnung der einzelnen k Werte auftritt und von der Änderung des Dissoziationsgrades wegen der geringen Verdünnung durch die Disproportionierung herrührt, wurde nicht korrigiert.

Diese Untersuchungsergebnisse widersprechen den Deutungen des Disproportionierungsvorganges mittels kinetischer Reaktionsgleichungen zweiten und höheren Grades. Wenn die Cr^{IV}-Konzentration in der Reaktionsgleichung unter höheren Exponenten stünde, wäre nach dem Zeitpunkt der Verdünnung die halbe Extinktion der fünffach verdünnten Lösung kleiner als die der zehnfach verdünnten. Unsere Messergebnisse ergaben aber gerade das Gegenteil.

Die Frage des Cr^{IV}-Molekülzustandes zeigte sich in einem neuen Lichte, als es uns in einigen Vorversuchen gelang tiefbraune Reaktionsmischungen der Chromatreduktion auch in phosphor- und perchlorsauren Lösungen gegebener Konzentration herzustellen. Im Falle der Perchlorsäure geschieht das schon in verhältnismässig niedrigkonzentrierten Säurelösungen. Es ist interessant, dass die Verfärbung in schwefelsauren Lösungen im bereits bekannten Gebiet von 70–85% auftritt. Bei Salzsäure konnten wir in keiner Säurekonzentration eine Verfärbung feststellen. Diese Versuche weisen darauf hin, dass die ewähnten Oxysauren die Bildung des Cr^{IV} beeinflussen. Wenn dies so ist, dann könnte die Reaktion nicht mit dem Auftreten der Trimere in *Iso*polysäure, sondern in Heteropolysäuremolekülen ihre Deutung finden. Die Diffusionsversuche[1] wiesen schon darauf hin, dass in 70%-iger schwefelsaurer Chromatlösung stark polymerisierte Chromsäure auftritt. Wir setzen unsere diesbezüglichen, sowie die spektrophotometrischen Untersuchungen weiter fort, wollen aber schon jetzt die Aufmerksamkeit auf diese von vielen Seiten zu bearbeitenden Fragen lenken.

VERSUCHE ZUR MESSUNG DES Cr^{IV}-ABSORPTIONSSPEKTRUMS

Wenn man das Absorptionsspektrum einer mit mittlerer Geschwindigkeit disproportionierenden Komponente bestimmen will und die Reaktionsprodukte ebenfalls Licht absorbieren, so kann die schematische allgemeine Gleichung

$$xX = aA + bB + cC + \cdots$$

in Form der ausintegrierten kinetischen Gleichung folgendermassen ausgedrückt werden:

$$E_t - E_\infty = X_0(1 - \frac{a}{x}\varepsilon_A - \frac{b}{x}\varepsilon_B - \frac{c}{x}\varepsilon_C \ldots)e^{-kt}$$

wo E_t die zum Zeitpunkt t und E_∞ die nach Ablauf der Reaktion gemessene Extinktion bedeutet. Die grossen Buchstaben drücken die Konzentration der am Reaktionsverlauf teilnehmenden Komponenten, die kleinen die entsprechenden Molzahlen aus. X_0 bedeutet die Konzentration der disproportionierenden Komponente zum Zeitpunkte $t = 0$, ε hingegen die entsprechenden Extinktionskoeffizienten. k ist die Reaktionsgeschwindigkeitskonstante. Die Gleichung kann im Falle der Cr^{IV}-Disproportionierung in folgender Form ausgedrückt werden:

$$\log \frac{E_t - E_\infty}{C_{IV,0}} = \log (\varepsilon_{IV} - \tfrac{2}{3}\varepsilon_{III} - \tfrac{1}{3}\varepsilon_{VI}) - \frac{kt}{2{,}303}$$

Die Ableitung besitzt nur dann Gültigkeit, wenn

(1) die Disproportionierung mit Hilfe einer Reaktion ersten Grades ausgedrückt wird,

(2) das Lambert-Beer'sche Gesetzt für jede Komponente zutrifft und

(3) wenn parallel mit der Disproportionierung keine Nebenreaktionen ablaufen.

Schon in unserer ersten Arbeit wiesen wir darauf hin, dass die Gleichung die Extinktionsberechnung leicht disproportionierender Reaktionskomponenten ermöglicht. Diese Feststellung ergänzten wir in unserer jetzigen Arbeit mit der Annahme des Depolymerisationsgleichgewichtes, was nach sich zieht, dass das Lambert-Beer'sche Gesetz scheinbar seine Gültigkeit verliert. Obzwar der Dissoziationsgrad bei jeder Cr^{IV}-Konzentration berechnet werden kann und damit die Korrektion des Lambert-Beer'schen Gesetzes möglich wäre, ist es doch nicht möglich das Absorptionsspektrum des Cr^{IV} genau zu bestimmen, und zwar deshalb, weil die Lichtabsorption der Dissoziationsprodukte unbekannt ist. Es kann bloss der qualitative Ablauf der Extinktionskurve angegeben werden.

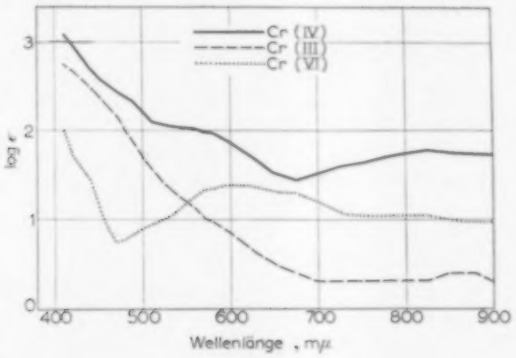

Abb. 2.

In Abb. 2 trugen wir die auf Grund der kinetischen Messungen unmittelbar errechneten und nicht korrigierten logarithmischen Extinktionswerte des Cr^{IV} auf. Die Werte beziehen sich nicht auf die wirklichen molaren Extinktionen, sondern geben bloss ein qualitatives Bild des Cr^{IV}-Spektrums. Die ebenfalls dargestellten Cr^{III}- und Cr^{IV}-Spektren, in 78%-iger Schwefelsäure, drücken die wahren dekadischen molaren Extinktionskoeffizienten aus und sollen als Vergleich zum Spektrum des Cr^{IV} dienen.

J. Inorg. Nucl. Chem., 1958, Vol. 7, pp. 418 to 420. Pergamon Press Ltd., London

INVESTIGATION OF THE BLACK SOLID FORMED ON REACTION OF URANIUM METAL WITH HYDROCHLORIC ACID

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Abstract—The oxidation state of uranium in the black solid formed by reaction of uranium metal with 6 N HCl in an atmosphere of nitrogen has been found to be 2·7 ± 0·1 by direct analysis. This was substantiated by an indirect method based on measurements of the hydrogen evolved and the uranium in solution. Only a trace of chloride was found in the solid. An oxidation state of 2·67 corresponds to an oxide, U_3O_4. X-ray analysis showed no uranium metal present. Lines of UO_2 were visible, as would be expected because of the ease of oxidation of the substance, and lines were present that cannot be assigned to any known oxide of uranium.

BLACK solids are formed by the reaction of uranium metal with hydrochloric acid, by the reduction of uranyl salts and by the anodic oxidation of uranium metal in the presence of certain electrolytes. Investigations were planned for all of these and the first one studied was that formed by the reaction of the metal with acid. In this case the formation of a dark solid as well as U^{3+} and U^{4+} is well known,[1] and studies have been made on the average oxidation state of the uranium in the total reaction product.[2] The work presented here concerns the oxidation state of uranium in the solid.

The metal used was polished uranium sheet containing less than 0·1 per cent impurities. An apparatus was devised in which the reaction of the metal with 6 N HCl, previously cooled in an ice bath and saturated with nitrogen, the filtration of the solid by suction on a fritted glass plate, and the washing of the solid with 6 N H_2SO_4 were carried out in an atmosphere of nitrogen. For coagulation of the solid before filtration, the reaction mixture was allowed to stand 24 hr and in that time any U^{3+} in solution was oxidized to U^{4+} by H^+. Only a trace of chloride was found in the solid.

An excess of standard ceric ammonium sulphate solution was used to dissolve the solid and convert the uranium to UO_2^{++}, the excess $Ce^{(IV)}$ being determined by back titration with standard ferrous ammonium sulphate. The number of moles of uranium present was found by the standard procedure of reducing the UO_2^{++} to U^{4+} (Jones reductor) and by titration of the U^{4+}, after aeration, with the ceric solution. It should be noted that any Fe^{3+} in the standard ferrous solution, as well as the Fe^{3+} produced by the reaction of Fe^{++} with Ce^{4+}, is reduced in the reductor and reoxidized by Ce^{4+}.

From the number of equivalents required to oxidize the uranium of the solid to UO_2^{++} and the number of moles of uranium found present, the oxidation number of

[1] *The Actinide Elements* (edited by G. T. SEABORG and J. J. KATZ) NNES, Div. IV, Vol. 14A, p. 138. McGraw-Hill, New York (1954).
[2] J. J. KATZ and E. RABINOWITCH, *The Chemistry of Uranium* p. 168. McGraw-Hill, New York (1951).

the uranium was calculated as 2·7 ± 0·1. This was the average of 4 runs (Table 1) and corresponds to a formula U_3O_4.

The oxidation number of the uranium in the filtrate was found to be 4·00 ± 0·05 and the amount of uranium can be obtained by subtracting that in the black solid from the quantity of metal used. The average oxidation state of the total uranium, that in the solid plus that in the filtrate, can be readily calculated from the data in Table 1. In Run no. 3 it was found to be 3·72, 3·71 in Run no. 4 and 3·86 in Run no. 2. There was some loss of solid in Run no. 1.

TABLE 1.—OXIDATION STATE OF URANIUM IN BLACK SOLID FORMED BY THE REACTION OF APPROXIMATELY 1 g OF URANIUM METAL WITH 10 ml OF 6 N HYDROCHLORIC ACID

Run no.	Wt. U (g)	Milliequivalents required to oxidize solid to UO_2^{++}	Milliequivalents required to oxidize U^{4+} to UO_2^{++}	Millimoles U in solid	Stages of oxidation from U of solid to UO_2^{++}	Oxidation number of U in solid
1	0·4438	0·2991	0·1754	0·0877	3·41	2·59
2	0·9829	1·514	0·9426	0·4713	3·21	2·79
3	1·1418	3·264	1·979	0·9895	3·29	2·71
4	1·1611	3·517	2·142	1·071	3·28	2·71

This average oxidation number was checked by measurement of the hydrogen evolved in the reaction of the metal with 6 N HCl in a gas-burette type of apparatus, precautions being taken to eliminate air. The volume of the gas, temperature, and vapour-pressure of the HCl solution were all obtained when the uranium in solution was U^{4+}. The average oxidation of the uranium thus obtained was 3·66 ± 0·01 which corresponds fairly well with the average charge calculated from the data of Table 1. The reliability of the method and apparatus was checked against iron and aluminum. For the former, the charge obtained was 1·99 and for the latter, 2·96.

The apparatus used in isolation of the solid was of such construction that the dark substance could be washed with alcohol and ether in the presence of nitrogen, pumped dry and introduced into capillary tubes for X-ray analysis. The analyses were carried out with a North American Philips Powder Camera. Lines of uranium metal were absent; lines of UO_2 were present, indicating some oxidation of the powder, and lines were also present that could not be assigned to those of any other uranium oxide recorded.

The black solid produced by electrolytic reduction of uranyl chloride in HCl *solution.* It was thought possible that the solid that is formed on the electrolysis of a uranyl chloride solution in hydrochloric acid might have the same composition as that produced by the reaction of the metal with acid.

A series of runs were made in an apparatus closely resembling that of ROSENHEIM and LOEBEL,[3] the reaction mixture being protected from air by use of CO_2. The acid concentration was varied from 8 N to 1½ N. The dark colloidal precipitate formed after the uranium passed through the 4+ stage. Finally, the solution appeared colourless although the solid was suspended throughout. The black substance was so

[3] ROSENHEIM and LOEBEL, *Z. anorg. Chem.* **57**, 234 (1908).

finely divided and so reactive toward air that a satisfactory method of separating it from solution was not found.

Several runs, however, were made with rather dilute HCl ($1\frac{1}{2}$ N) so that the analysis of the uranium could be carried out directly on the diluted mixture without the chloride appreciably reducing the dilute Ce^{4+}. In these runs the cathode chamber contained 90 ml of acid and from 0·5 to 3 g of $UO_2Cl_2H_2O$. The amperage was 0·9, the current density was 0·0233 A/cm² of mercury surface, and the time of electrolysis was varied from 3 to 4 hr. The number of coulombs used was, therefore, many times that theoretically necessary to reduce the uranium present through 4 stages of oxidation. For the analysis only a portion of the cathode mixture was used which was conveyed, protected by CO_2 from the atmosphere, directly into dilute Ce^{4+} solution. The oxidation state of the uranium as found in 5 runs was $3{\cdot}08 \pm 0{\cdot}04$.

Acknowledgements—The author wishes to thank Professor D. P. SHOEMAKER and Mr. P. H. METZGER for the analysis by X-rays.

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J. Inorg. Nucl. Chem., 1958, Vol. 7, pp. 421 to 425. Pergamon Press Ltd., London

LETTERS TO THE EDITORS

On the structure of $PtS_4N_4H_2$

(*Received* 28 *August* 1958)

In a recent paper[1] the crystal structure of a compound with the assumed formula PtS_4N_4 was presented. The authors also reported a private communication by Piper who suggested the formula $PtS_4N_4H_2$, and they stated that a decision between the two formulae was not possible by X-ray methods. The formula $PtS_4N_4H_2$ is, however, now generally accepted,[2,3] and we have therefore tried to find where the hydrogen atoms might be situated on the molecule. For that purpose we have

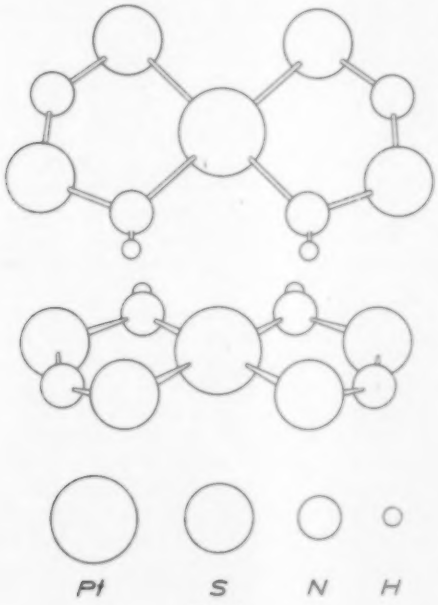

Fig. 1

built a space model of the structure which indicates that it is almost certain that the hydrogen atoms are attached to the nitrogen atoms nearest to platinum. In the earlier paper,[1] some rather long intermolecular distances are reported, which were assumed to be due to the inaccuracy of the structure determination. These long distances are very naturally explained by a structure with an ψNH group bonded to platinum. All other van der Waals distances have normal values. The packing of one molecule with another is shown in Fig. 1, assuming rather arbitrarily that the hydrogen atoms

[1] I. Lindqvist and J. Weiss, *J. Inorg. Nucl. Chem.* **6**, 184 (1958).
[2] T. S. Piper, *Chem. & Ind.* **37**, 1101 (1957).
[3] J. Weiss and M. Becke-Goehring, *Z. Naturf.* **13B**, 198 (1958).

are exactly in the same plane as the rest of the molecule. Any structural suggestion based only on space considerations must be slightly arbitrary and we do not think that it is possible to deduce more from the crystal structure determination. We hope, however, that the structure will be confirmed by proton resonance measurements by PIPER, by studies of new chemical reactions or by structure determinations of related compounds by WEISS and BECKE-GOEHRING. The theoretical calculations reported to be in progress[1] will not be continued until the structure of the molecule has been definitely established.

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Anion-exchange studies with actinium and lanthanides in nitrate solutions

(*Received 5 August* 1958)

IN a previous paper we reported that the lanthanides are slightly adsorbed by anion-exchange resins, such as Dowex-1, from concentrated nitric acid solutions.[1] Further experiments with praseodymium have shown that this element adsorbs more strongly on Dowex-1 from nitrate solutions than from the acid media.[2] This adsorption was found to increase with the nature of the cation of the supporting nitrate solution in the order: $H < NH_4 < Li < Ca < Cu < Fe < Al$.

These results were extended by MARCUS for a number of lanthanides and successful separations of these elements were achieved with the anion-exchange resin in lithium nitrate solutions.[3]

In the present communication we report a study on the anion-exchange behaviour of actinium, undertaken with the aim of separating trace-amounts of this rare earth like element from weighable quantities of its homologue lanthanum.

The separation of actinium and lanthanum was investigated in 30 cm × 0·24 cm² columns of Dowex-1, 8% DVB, 50–100 mesh, in the nitrate form. Actinium-228 (MsTh II, β, γ, 6·13 hr period) was extracted from radium-228 (MsTh I, β, γ, 6·7 year period) according to the procedure of HAISSINSKY.[4] The purity of the radioelement was controlled by period measurements and by its γ-energy spectrum, determined in a NaI(Tl) scintillation spectrometer. Activity measurements were made in a scintillation counter. Lanthanum nitrate, prepared from its oxide (Johnson, Matthey Specpure), was detected colorimetrically using sodium alizarine sulphonate.[5]

The nitrates were dissolved in concentrated lithium nitrate solution and introduced in the column. Elution was carried with more dilute lithium nitrate and its course followed by sampling the effluents in volumes of 3 ml, which were analysed radiometrically for actinium and colorimetrically for lanthanum. The results obtained in a typical experiment are shown in Fig. 1. In this experiment 3 ml of an 8·5 M $LiNO_3$ solution with tracer actinium and 30 mg of $La(NO_3)_3$ were slowly introduced into the column, which has been pretreated with 8·5 M $LiNO_3$. Elution was carried out with 4·4 M $LiNO_3$ at a flow rate of 0·4 cm/min.

From column experiments and equilibrium measurements with actinium the following values were obtained for the distribution coefficient D_e[= [(Ac) resin vol. sol.]/[(Ac) sol. vol. resin]] as a function of the molarity of lithium nitrate.

M_{LiNO_3}	2·5	3·1	3·6	4·0	4·4	5·6
D_{Ac}	1·7	3·1	5·1	6·1	10·2	17·5
D_{La}	—	5	10	—	20	—

[1] J. DANON, *Ann. Acad. Bras. Cien.* **28**, XLVII (1956).
J. DANON, *J. Inorg. Nucl. Chem.* **5**, 237 (1958).
[2] J. DANON, To be published.
[3] Y. MARCUS, Private communication (1958).
[4] M. HAISSINSKY, *C.R. Acad. Sci., Paris* **196**, 1778 (1933).
[5] E. B. SANDELL, *Colorimetric determination of traces of metals*. Interscience, New York (1950).

The results of Marcus have shown that the adsorption of the lanthanides by the anion-exchange resin, at a fixed lithium nitrate concentration, increases in the sequence Yb < Tb < Eu < Sm < Pm < Nd < Pr < Ce < La, which is also the order of increasing ionic radius or increasing basicity in the series.[2] The adsorption position of Ac in this sequence falls approximately between Sm and Nd. This is somewhat unexpected, since the ionic radius of Ac^{+3} (1·11 Å) is larger than that of La^{+3} (1·06 Å) and its chemical properties are in general those of a more basic element.[6] Moreover, we found that the adsorption positions of the lower homologues of lanthanum, Y and Sc, are approximately those expected from their relative basicities: Sc < Yb < Y < Tb < ... < La.

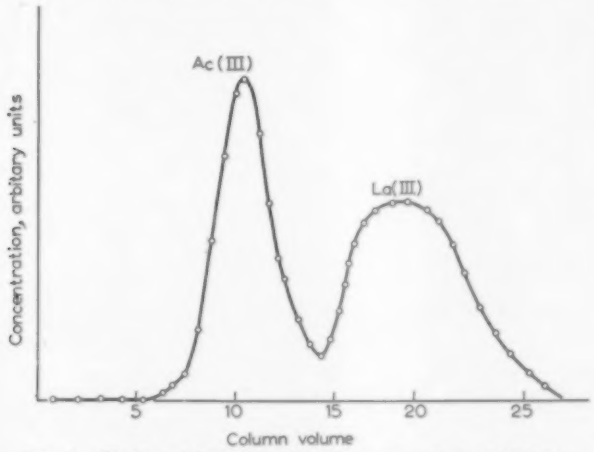

FIG. 1.—Elution of Ac and La from Dowex-1 with 4·4 M $LiNO_3$.

An anomalous behaviour of Ac with respect to its basicity was reported many years ago by CURIE and TAKVORIAN.[7] These authors observed that during the fractional crystallization of the lanthanon magnesium double nitrates all the actinium concentrates between Sm and Nd instead of accumulating with the more basic fractions. The remarkable analogy with the adsorption position of Ac suggests that the solubility of these double nitrates may be correlated to the adsorption of the lanthanides by the anion-exchange resin. Thus, the solubility of these salts (g/100 ml H_2O) increases in the order[8] La < Ce < Pr < Nd < Sm, which is the reverse of the adsorbabilities of these elements by the resin. Crystalline double nitrates are not obtained with the heavier lanthanides, which is consistent with their low adsorbabilities

A meaning for these correlations can be given by assuming that the adsorption by the anion-exchange resin is determined by the stability of the nitrato complexes. On this basis, the solubility of the double nitrates of the lanthanides and of actinium decreases with the increase in the tendency toward the formation of nitrato complexes in the series. Similar relations between solubility and complex stability have been reported by WILLIAMS for the nitrates of the alkali-earth metals.[9]

A comparison between the anion-exchange behaviour of actinium and americium (Am^{+3})[2] (0·99 Å) shows these elements adsorb from $LiNO_3$ solutions in the order Ac < Am. Spectrophotometric and ion-migration studies[10] suggest that Am^{+3} is more complexed by the nitrate ion than Pu^{+3}. The adsorbability of these actinides will probably fall in the sequence Ac < Pu < Am, which is the order of decreasing ionic radius in the series and the reversal of that observed with the lanthanides. Differences in the tendency toward complex formation between elements of comparable ionic radius such as the lanthanides and the actinides have been attributed to modifications in the character of the metal ligand bonds in the two series.[11] For the nitrate systems, useful information about this

[6] J. J. KATZ and G. T. SEABORG, *The Chemistry of the Actinide Elements* p. 15. Methuen London (1957).
[7] M. CURIE and S. TAKVORIAN, *C.R. Acad. Sci., Paris.* **198,** 1687 (1934).
[8] R. C. VICKERY, *Chemistry of the Lanthanons* p. 116. Butterworths, London (1953).
[9] R. J. P. WILLIAMS, *J. Chem. Soc.* 3770 (1952).
[10] G. N. YAKOLEV and V. N. KOSYAKOV, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva,* 1955, Vol. 7, p. 363. United Nations (1956).
[11] R. M. DIAMOND, K. STREET, JR., and G. T. SEABORG, *J. Amer. Chem. Soc.* **76,** 1461 (1954).

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question could be derived from systematic studies on the infra-red spectra of the double nitrates of the lanthanides and of actinides with a bivalent cation, analogous to those done by GATEHOUSE *et al.* for $Zn_3Pr_2(NO_3)_{12}24H_2O$ and other nitrato complexes.[12]

The author thanks Dr. G. BOUISSIÈRES and M. HAISSINSKY for a MsTh source and Dr. L. MARQUES for the measurements with the scintillation spectrometer. This work was carried out under the auspices of the Conselho Nacional de Pesquisas.

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[12] B. M. GATEHOUSE, S. E. LIVINGSTONE and R. S. NYHOLM, *J. Chem. Soc.* 4222 (1957).

Some observations on phosphorous(III) *iso*cyanate

(*Received* 6 *June* 1958)

PHOSPHORUS(III) *iso*cyanate was first prepared by FORBES and ANDERSON[1] by metathesis of PCl_3 and AgOCN in benzene. The compound is a colourless liquid which polymerizes rapidly at room temperature to give a white solid of unknown molecular weight which possesses the same empirical formula as the liquid. We have studied $P(NCO)_3$ as a liquid that might offer unusual solvent properties for a particular application. However, its great tendency to polymerize and its sensitivity toward moisture limit the usefulness of $P(NCO)_3$ as a solvent.

Properties of $P(NCO)_3$ are given in Table 1. $P(NCO)_3$ exhibits solvent properties commonly

TABLE 1.—PROPERTIES OF $P(NCO)_3$

	FORBES and ANDERSON	This work
Melting point (°C)	−2	ca. −2*
Boiling point (°C)	169·3	169
		45–50/40–60 mm
Density (g/ml)	1·439 (25°C)	1·450 (26°C)
Refractive index	1·532 (20° C, white light)	1·525 (26°C, sodium light)
Specific conductivity, 25°C (ohm^{-1})		$1·89 \times 10^{-5}$

* Liquid exhibits tendency to supercool

associated with organic liquids. The solubilities of a number of substances were observed qualitatively in $P(NCO)_3$, and results are shown in Table 2. The behaviour of iodine in $P(NCO)_3$ is noteworthy in that a reddish-brown solution results, indicating that $P(NCO)_3$ is an active solvent[2] towards iodine (i.e. co-ordinates with it in compound formation). The observations on I_2-$P(NCO)_3$ solutions will be the subject of a forthcoming paper.

FORBES and ANDERSON postulated that $P(NCO)_3$ should possess the *iso*- rather than the normal cyanate structure. We have confirmed the *iso*- structure for $P(NCO)_3$ by measurement of the infra-red spectrum of the compound in the region 2–15 μ in the liquid and gaseous states and in the solvent

TABLE 2.—SOME SOLUBILITIES IN $P(NCO)_3$

Insoluble	Soluble without reaction	React violently	React slowly
$AlCl_3$	$(CH_3)_2CO$ (cold)	H_2SO_4 (anhyd)	$(C_2H_5)_2O$
Fe	C_6H_6	H_2O	C_2H_5OH
$PbCrO_4$	$CHCl_3$	$AgNO_3$	CH_3OH
Mg	C_2H_5I	CH_3COOH	Na_2S
P (red)	$C_6H_5NO_2$	CH_3CHO	$(CH_3)_2CO$ (warm)
P (white)	C_6H_5OH		alkali metals
KBr	C_2H_7COOH		I_2
K_2CO_3			
KCl			
KOCN			
KCN			
KOH			
KI			
KIO_3			
$KClO_4$			
K_2HPO_4			
K_3PO_4			
KSCN			
AgOCN			
$NaC_2H_3O_2$			
Na_2HAsO_4			
$NaNO_2$			
$NaNO_3$			
Na_2SO_4			
S			
Zn			

CS_2. In each case, a strong absorption band at 4·5 μ was noted, characteristic of the *iso*cyanate grouping.[3]

Acknowledgement—We wish to thank the Research Corporation for financial support during part of this study.

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(1) G. S. FORBES and H. H. ANDERSON, *J. Amer. Chem. Soc.* **62**, 761 (1940).
(2) K. KLEINBERG and A. W. DAVIDSON, *Chem. Rev.* **42**, 601 (1948).
(3) H. HOYER, *Ber. Dtsch. Chem. Ges.* **89**, 2677 (1956).

BOOK REVIEW

Inorganic Syntheses. Volume V, Editor-in-Chief T. MOELLER, Inorganic Syntheses Series. McGraw-Hill, New York, 1957. xiv + 265 pp., $6.00

THIS volume is a welcome addition to a well-established series concerned with the preparation of inorganic substances. As in previous volumes each synthesis has been checked in a laboratory other than that in which it was developed, and this has undoubtedly increased the usefulness of the procedures described. With the appearance of this book the editor, contributors and publisher have made a definite contribution to preparative inorganic chemistry, but the choice of some of the syntheses included calls for adverse comment.

Thus, as in previous volumes of the series a few of the preparations described are for compounds commercially produced. In this reviewer's opinion the advantage of including descriptions of how to synthesize substances as readily available as sodium hydride or ethyl orthoborate is doubtful, even allowing for the possibility that the editors of *Inorganic Syntheses* wish to provide books suitable in part for the teaching of synthetic inorganic chemistry.

Also included in this volume are descriptions for preparing certain compounds of negligible importance. This is especially surprising when many of the interesting substances that have never been mentioned in *Inorganic Syntheses* are considered. Thus, for example, descriptions are given for the preparations of trimethylamine-boron trifluoride and trimethylamine-boron trichloride. The significance of these boron halide addition compounds is trivial compared with that of the various known trialkylboranes, borazoles, and borohydrides, yet syntheses and reactions of these three classes of compounds have never appeared in the series. In passing, it may be mentioned that in the section concerned with the preparation of trimethylamine-boron trifluoride it is incorrectly stated that the adduct is associated in the vapour phase.

Vols. III and IV of *Inorganic Syntheses* both contained methods for preparing certain organometallic compounds of the Group IVB elements. Vol. V, with its several syntheses for organogermanium compounds, continues this emphasis on organo-metal derivatives of the Group IVB elements. Such syntheses are certainly worthy of inclusion. In recent years, however, many interesting new organo-metal compounds of other elements have been described, and a judicious inclusion of a few of these substances would have greatly increased the value of this latest volume of *Inorganic Syntheses*.

With this book, the foregoing criticisms notwithstanding, the editor and publisher are to be commended for continuing to fill partially, and at a reasonable price, an important gap in our scientific literature.

F. G. A. STONE

ERRATA

D. P. GRADDON, *J. Inorg. Nucl. Chem.* **7**, 73 (1958).
In the sub-title of this paper "DECARBOXYLIC" should read "DICARBOXYLIC".

Abstracts from 2nd U.N. Conference, Geneva, September 1958, *J. Inorg. Nucl. Chem.* **7**, 164–186 (1958).

Abstract P/1605 by Y. MARCUS (Israel).

P. 176, first column; the second line should read "acid (HA) and phosphoric acid–mono-".

Papers to be published in future issues

F. K. LOTGERING: Topotactical reactions with ferrimagnetic oxides having hexagonal crystal structures—I.

W. G. GEHMAN and W. C. FERNELIUS: The mechanism of racemization of the tris(ethylenediamine) cobalt(III) cation.

G. JANDER und G. WINKLER: Acetamid als nichtwässriges ionisierendes Lösungmittel—I. Konduktometrische Titrationen in geschmolzenem Acetamid.

G. JANDER und G. WINKLER: Acetamid als nichtwässriges ionisierendes Lösungmittel—II. EMK-acetamid Messungen und potentiometrische Titrationen in geschmolzenem Acetamid.

G. JANDER und G. WINKLER: Acetamid als nichtwässriges ionisierendes Lösungmittel—III. Lietfahigkeit und Stärke von Elektroylten in geschmolzenem Acetamid.

J. HALPERIN, J. O. OLIVER and H. S. POMERANCE: The thermal neutron absorption cross-section of ^{240}Pu.

F. M. BREWER, G. GARTON and D. M. L. GOODGAME: The preparation and crystal structure of gallium trifluoride.

NOBUYUKI TANAKA and TSUTOMA TAKAMURA: Spectrophotometric studies on thiocyanatocuprate(II) complexes in aqueous solution.

T. MOELLER, E. GULYAS and R. H. MARSHALL: Observations on the rare earths—LXVIII. Partial resolution of yttrium and gadolinium acetylacetonate by means of a chromatographic technique.

T. D. SMITH: The salts of organic phosphorus acids—I. The infra-red spectra of salts of di-*n*-butyl phosphate.

D. G. TUCK and G. A. WELCH: The properties of inorganic compounds in organic solvents—II. The ion exchange reactions of quadrivalent plutonium in diethylene glycol dibutyl ether.

R. H. FLOWERS, R. J. GILLESPIE and E. A. ROBINSON: Basic properties of the dioxides of group VI—I. Solutions of selenium dioxide in sulphuric acid and oleum.

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